THESIS FOR THE DEGREE OF LICENTIATE OF ENGINEERING

DIFFUSION OF IONS IN WOOD

Local concentration profiles of Li^+ ion in a single wood piece of Norway spruce

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To my father

Aswartha Narayana Kolavali

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ABSTRACT

Wood sourced from well managed plantations or forests, is a renewable material with many advantages over non-renewable (fossil) material, and also wood lignocelluloses are the only type of biomass that is a seasonal-independent product. In addition to direct utilization as a building material, major uses of wood are currently for making pulp and paper products, and fuel. Even with the combination of pulp, paper, and energy the paper industry has had low profitability for over the last few decades. Therefore, converting a chemical pulp mill into an Integrated Forest Products Biorefinery, in which higher value-added products such as ethanol, polymers, carbon fibers and diesel fuel are produced together with pulp and paper, seems to be a potentially profitable utilization.

Not only in the wood-based biorefinery applications, but also in the applications in which solid wood is treated with different kinds of chemicals, the wood material has to be impregnated with reactants. The impregnation of wood material with chemicals can be divided into advective (penetration) and diffusive (diffusion) mass transport. Little is known about the diffusive mass transport partly because of difficulties in the determining the relevant diffusivities for a given system. In the present study, an experimental methodology has been developed to measure the concentration profiles of cations as a function of wood piece dimensions, impregnation time, temperature, and wood structure. Cation concentration can be measured at any position in an impregnated wood piece (local concentration profiles). The impregnation of Norway spruce wood with lithium chloride was investigated in this study. The impregnated wood pieces were cut mechanically into cubes, which were then sliced into ~0.3 mm thick slices using a microtome, and the eluate of these slices in HNO_3 was analyzed using Flame Atomic Emission Spectroscopy. This approach was found to be more appropriate than traditional methods based on either electrochemical potential or flux measurements for studying the diffusion of chemicals into wood.

It was observed that the method gives reasonable results, and is able to detect defects (micro-cracks) and other phenomena that influence the mass transport of ions in wood, e.g. the Donnan effect. For the experimental conditions chosen, the effects of temperature and differences between sap- and heartwood on the Li^+ ion concentration profiles of Norway spruce wood were less significant than the effect of impregnation time.

Keywords: diffusion; Donnan effect; experimental methodology; impregnation; lithium chloride; local concentration profiles; micro-cracks; Norway spruce; wood.

LIST OF PUBLICATIONS

This thesis is based on the research work presented in the following papers. The manuscripts can be found at the end of the thesis.

I. Determination of the diffusion of monovalent cations into wood under isothermal conditions based on LiCl impregnation of Norway spruce
Reddysuresh Kolavali and Hans Theliander
Holzforschung 2013; 67(5):559-565

II. Experimental determination of the diffusion of monovalent cation into wood: Effects of temperature and impregnation time on concentration profiles
Reddysuresh Kolavali and Hans Theliander
J-FOR, Journal of Science & Technology for Forest Products and Processes
(Manuscript under review)

Results relating to this work have also been presented at the following conferences:

Experimental determination of the diffusion of monovalent cation into wood under isothermal conditions
Kolavali Reddysuresh and Hans Theliander
(Poster presentation)
In conference proceedings. EWLP 2012, 12th European Workshop on Lignocellulosics and Pulp, Espoo, Finland, August 27-30, 2012, pp 476-479.

Experimental determination of the diffusion of monovalent cation into wood: Effects of temperature and impregnation time on concentration profiles
Kolavali Reddysuresh and Hans Theliander
(Oral presentation)
In conference proceedings. ISWFPC 2013, 17th International Symposium on Wood, Fiber and Pulping Chemistry, Vancouver (BC), Canada, June 12-14, 2013, Process Chemistry Track, Chemistry of the fiber wall and its components.

Contents

1. INTRODUCTION

Petroleum and other fossil energy resources are considered to be nonrenewable carbon resources because of their long geologic recycle (or renewable) times (~ 200 million years) as compared with biomass (~ <1 to 80 years) feedstocks, which are renewable and carbon neutral resources (Liu et al., 2006). In recent years, several types of potential biomass feedstocks have been identified and it has been proposed that each biomass type has to be processed in a specific way to produce sustainable materials, chemicals, and energy (Schlosser and Blahusiak, 2011) with a high efficiency. Wood lignocelluloses are the only type of biomass that is a seasonal-independent product, and lignocelluloses are also the most abundant biomass on earth, accounting for an annual production of ~170 billion metric tons in the biosphere. In Sweden, woody biomass resources have provided the basis for significant industrial activities for several centuries. Pulp and paper and sawn timber products have dominated the use of woody raw material, but use for energy purposes has grown stronger during recent decades. However, increasing competition from countries with fast-growing forests makes it necessary to increase competitiveness and to find new and highly refined products to complement the existing pulp-based products.

The 'biorefinery' is the most popular concept in this context for converting forest biomass to energy and chemicals. According to the National Renewable Energy Laboratory (NREL), 'a biorefinery is a facility that integrates conversion processes and equipment to produce fuels, power, and chemicals from biomasses' (Fernando et al., 2006). Biomass is composed of carbohydrates, lignin, proteins, fats, and to lesser extent various other chemicals, such as vitamins, dyes, and flavors. Thus the main goal of a biorefinery is to transform such plentiful biological materials into useful products applying a combination of technologies and processes. The operations should be designed to maximize the valued extractibles while minimizing waste streams by converting low-value high-volume intermediates such as ethanol and renewable diesel into energy. High-value products such as plastics, resins, adhesives, carbon black are intended to enhance the profitability, while high-volume fuels help to meet the global energy demand. Thus the biorefinery (renewable biomass as feedstock) is in many ways analogous to the petroleum refinery (nonrenewable petroleum as feedstock), whereby a single feedstock is fractionated to a multitude of commodity products depending on societal necessity.

The pulping industry is the most developed chemical technology for processing wood, and to some extent it is already a biorefinery in which energy, cellulosic fibers, and minor amounts of turpentine and tall oil are produced from wood. The interest for the biorefinery concept in this area has increased significantly in the recent years mainly due to: (a) the trend of increasing cost for wood and decreasing prices for pulp and paper; (b) greater competition from low cost producers of pulp and paper in South America and Asia; (c) Higher energy prices and new policy instruments that affect the production of materials such as non-petroleum-based materials and chemicals, and renewable materials.

The three major components of wood are cellulose (40-50%), hemicelluloses (30-35%), and lignin (20-30%). In a typical chemical pulp mill, wood is mainly used to produce fibers (cellulose and some hemicellulose) and electricity/steam (hemicellulose and lignin).The wood material efficiency in such chemical pulp mills is only about 40-55 % and cellulose as the main component in the final product. The other wood components such as lignin and hemicelluloses are degraded to various extends during the process and are just burned to recover latent energy in the recovery boiler (Sixta, 2006).But with the evaluation of biorefinery concept, several potential end-products have been proposed to generate from both lignin and hemicelluloses. These products can serve as a response to a greater sustainability demands as well as be of economic interest. Some of these products have already been commercialized and others are at the research and development stage (Ragauskas et al., 2006). Therefore it is believed that the concept of biorefinery will play a significant role in forest clusters worldwide.

Not only in the fractionation of different wood components for the wood-based biorefinery applications, but also in the applications in which solid wood is treated with different kinds of chemicals such as preservatives, fire retardants, dimension stabilizing chemicals, and pulping chemicals; chemicals must be transported into wood prior to a reaction. Thus the wood has to be impregnated with the reactants, and therefore an understanding of the conditions that control the mass transfer of liquids into wood is of great importance in wood processing technology. The impregnation of wood material with chemicals can be divided into advective (penetration) and diffusive (diffusion) mass transport. Penetration is defined as the flow of liquor into the gas-filled voids of the wood pieces under the pressure gradients, and diffusion is defined as the transport of chemical ions through the liquid inside the wood pieces under the influence of concentration gradients. In fresh wood both mechanisms occur at the same time, but in certain cases most of the chemicals are transferred into wood by diffusion especially if chemicals are consumed via reactions inside the wood piece and thus develop a concentration gradient. Little is known about the diffusive mass transport partly because of the difficulties in the determining the relevant diffusivities for a given system. Consequently, the phenomenon that takes place during the diffusion of chemicals into wood needs to be understood better. Moreover, penetration occurs very fast, but diffusion is the much slower phenomenon. Therefore diffusion is the controlling mechanism in many wood conversion processes. Proper impregnation of wood with chemicals will be of great importance for economically viable and efficient processes, e.g. the wood-based biorefinery process, since homogeneous impregnation increases the uniformity of the treatments and reduces reaction times. Moreover, the price of wood is the largest single cost factor in today’s pulp mills and may most likely be true in future wood-based biorefineries. For this reason also it is of vital importance to achieve maximum yield with wood fibers that have optimum properties.

2. OUTLOOK: WOOD AS A RAW MATERIAL

Wood sourced from well managed plantations or forests, is a renewable material with many advantages over non-renewable material. The fundamental challenge for forest based industry is how to supply more wood products with less impact on the environment. This challenge spans the whole supply chain, from where and how wood is grown and harvested to how intelligently and proficiently it is processed, used, and reused. The demand for forest products, e.g. products derived from woody biomass, are determined by a number of factors, such as: population, economic progression, and changes in demographics; technological change and environmental issues. Millions of people are coming out of poverty and joining the middle classes in developing countries such as China, India, and Brazil, and their increasing purchasing power signifies a great opportunity to make products that these populations require (Espinoza and Lagaurda-Mallo, 2013). In most of the developing countries, the major demand for forest products is as fuel wood. But as the Gross Domestic Product (GDP) increases in these countries, demand tends to shift towards industrial wood products such as sawn timber, panels, paper and paperboard (although per capita consumption will remain higher in Europe and North America). However, it will be difficult to expand wood production in Asia and the Pacific due to the high population density and competing land uses in these areas.

On the other hand, particularly in western countries, as a result of policies that encourage greater use of renewable energy, the most dramatic change will be the rapid increase in the use of wood as a source of sustainable materials, chemicals, and energy. An increasing awareness of the green aspects of wood also encourages governments and private enterprises to invest resources in the research and development of new materials and products derived from this renewable material, thus resulting in innovative and amazing applications.

Wood biomass is a carbon-neutral energy source that can provide energy for district heating, and/or with biochemical or thermochemical processes be converted into biofuels. Some examples of major inventions from wood-derived products and applications are described below:

2.1 Engineered wood products

Relative to its weight, wood is one of the strongest building materials. Its strength and ease of working; cutting, assembling using mechanical joints, adhesives, makes sawn timber ideal for many architectural and functional applications. Solid wood timbers are also used for rail road ties and various transportation structures such as bridges, sound barriers, guardrails, houses, and signposts (Jackson et al., 2001). But the use of engineered wood products has soared in the last few decades, and these products are replacing solid sawn timbers in residential and nonresidential construction. Wood is also the most eco-friendly building material. Cross Laminated Timber (CLT), is one such example of an innovative and promising products derived from solid wood (Espinoza and Lagaurda-Mallo, 2013). In addition to its light weight and extraordinary mechanical properties, CLT offers benefits such as thermal and acoustic insulations, great fire

retardant, and reduced installation time and costs. Wood modification can be defined as the processing of solid wood to facilitate a change in the chemical nature of the material or passive modification, where a change in properties is effected, but without an alteration of the chemistry of the material (Espinoza and Lagaurda-Mallo, 2013). Solid wood has been modified to reduce the biological availability of wood to wood degraders (such as white/brown- rot fungi) as well as to improve dimensional stability, durability, and mechanical properties. Different (Chemical/Thermal/Surface/Impregnation) wood modification methods have been identified, by referring to the changes that take place at the ultra-structural level of wood, i.e. cell wall level. Wood acetylation and Furfurylation treatment of wood (Larnoy et al., 2007) are examples of chemical and thermal wood modification methods respectively.

2.2 Pulp and Paper products

In addition to direct utilization as a building material, a current major use of wood is for making paper products. The pulp and paper industry produces different types of pulp from wood that is subsequently processed into paper. In the wood pulping process, the raw-cellulose bearing material, i.e. wood, is either chemically or mechanically defibrinated. Three different processes are common used for this purpose:

- Kraft (Sulphate) pulping: fibers are liberated from the wood matrix by treatment in a chemical solution at a high temperature; this process is well-known as the cooking process.
- Sulphite pulping: aqueous sulphur dioxide (SO_2 exists in different forms depending on the solution pH; HSO_3^-, SO_3^{2-}) is used in the cooking process.
- Mechanical pulping: the wood fibers are separated from each other by applying mechanical energy applied to the wood matrix. There are several types of processes that can be used for mechanical pulping, e.g. GroundWood (GW), Thermo Mechanical-Pulping (TMP), and Chemo-Thermo-Mechanical Pulping (CTMP). In chemi-mechanical pulping, the wood material is pre-softened with chemicals.

The Kraft pulping process is the dominant chemical pulping process today. In a chemical pulp (Kraft) mill, an aqueous caustic (NaOH) and sulfide (Na_2S) solution, known as white liquor, is used to cook the wood chips. Lignin and a large fraction of hemicelluloses are degraded and dissolved in the aqueous phase, known as black liquor. The black liquor is then burned to generate heat and recover caustic and sulfide. Usually, the paper industry utilizes cellulose for paper and lignin for energy, with some hemicellulose going to both purposes. Even with the combination of paper and energy, the paper industry has had low profitability for more than 15 years (Liu et al., 2006). Therefore the paper industry must look to inventiveness to change its overall profitability and improve its capability to persist. One such improvement is by converting a chemical pulp mill into an Integrated Forest Products Biorefinery (IFBR) in which higher value-added products such as ethanol, polymers, carbon fibers and diesel fuel can be produced together with pulp and paper (van Heiningen, 2007).

2.3 Wood-based biorefinery

Primary separation of the raw material into simpler components giving intermediates more versatile and easily used than the raw material itself is crucial to both petroleum- as well as bio-refinery concepts. Another key feature that is common to both refineries is the capability of generating a range of commercially useful products in a versatile manner that allows for rapid adjustment according to market requirements. Usage of renewable carbon, e.g. wood, eliminates an extra fossil-derived carbon dioxide burden to the environment and to greenhouse gas-driven global climate change. For this reason, well managed forests have significant potential to reduce green-house gas emissions by using forest material in biorefineries to create liquid fuels, electricity, and other products now being derived from nonrenewable carbon (fossil).

The wood species deliver a valuable starting point for a continuously operating biorefinery that can include many other biomass sources (Liu et al., 2006).The current global use of wood is approximately 3.6 billion m^3, of which more than half is employed in various forms of energy production. On the other hand, estimates of the global forest biomass that is potentially available for biorefining, calculated by assuming that 25% of the total annual surplus forest growth could be used, are in the range of 0.7–1.2 billion m^3 (Plackett, 2011). Therefore, wood is an enabling raw material for a continuously operating biorefinery: being a resource for continuous industrial operations year-round and during difficult agricultural crop production times.

Kraft pulp mills are the primary candidates to be transformed into biorefineries, as they have the infrastructure for processing woody biomass feedstock (Towers et al., 2007). Pulp and paper production at a Kraft (sulfate) pulp mill can be complemented with the use of lignin and hemicelluloses extracted from black liquor (the thick, dark liquid by-product of the Kraft pulping process) to derive various products as well as energy (Gellerstedt et al., 2010). Alternatively, pre-extraction and isolation of hemicelluloses have been suggested using different resources and processes, depending on the applications intended. Hemicelluloses may be pre-extracted by leaching from wood chips and conversion to monosugars through hydrolysis. These sugars can then be used to supplement cellulose in fermentation processes, e.g. to generate ethanol if genetically modified yeasts or bacteria are used, or targeting the production of value-added products, e.g. barrier films (Hansen and Plackett, 2008, Escalante et al., 2012, Alekhina et al., 2013) by means of acid hydrolysis, autohydrolysis, hot-water extraction, steam explosion, or alkali extraction could be a potentially profitable utilization.

2.4 Bio-energy

Over recent decades, western countries in particular have been developing policies to promote biomass-based energy. To illustrate this: the European Renewable Energy Council forecasts that, by 2020, bioenergy will make up about 13% of the total energy use in the EU, compared to approximately 7% for all other renewable energy, such as wind turbines, and solar panels combined. In the preindustrial era, renewable raw materials were the major source of energy and material use (Diercks et al., 2008). During the industrial revolution i.e. the 19^{th} century, the use of

coal increased sharply and became a key raw material in the chemical industry and in energy production. Later, in the 20th century, due to lower prices, simpler logistics, and the versatility in usage of oil and gas, there was a changeover in fossil fuel sources from coal to crude oil and natural gas. In view of the increasing price and the limited availability of crude oil and natural gas, biomass as a renewable source seems again to be a raw material base that will develop in future. There is a historical line of dominant resources used from local renewable resources to coal, coal gas, and tar industries to crude oil and natural gas in petroleum refineries and in the petrochemical industry. Currently a changeover to biomass in biorefineries and other renewable resources is of increased importance. Thus, although obtaining chemicals from wood is not something new, the technology for producing biofuels from forest biomass at a scale that can substitute a significant part of the petroleum-based fuels is new and attracting more and more research interest. Although the wood-based bioenergy sector is small compared to the pulp and paper industry, it is almost certainly the fastest growing market for wood and is set to push up the price of wood worldwide, thus making tree plantations and industrial logging ever more profitable (White, 2010).

2.5 Bio-materials and -chemicals

Non-traditional wood products have been developed to diversify wood markets and to contribute to developing a new bioeconomy (FPInnovations, 2013). Structural materials are strengthened with wood fibers, e.g. novel cellulosic membranes are an alternative to petroleum based resins. Novel cellulose-based insulation materials have been developed with enhanced environmental performance and better response to thermal and acoustic requirements than traditional materials (Cellulose Insulation Manufactures Association (CIMA), 2013).

In addition to the construction industry, other sectors have also benefitted from innovations in wood products. For example cellulosic biomaterials have been developed for isolating and making new cellulosic structures such as NanoCrystalline Cellulose (NCC), Cellulose Filaments (CF), and gels. The properties of these materials can improve a wide range of existing products, including pulp and paper, packaging, wood products, composite materials, bioplastics, paints, varnishes, inks, cosmetics, and textiles.

Materials that may be obtained from a wood biorefinery can complement the liquid fuel and specialty chemical portfolio. A future example is the conversion of part of the cellulose stream to nanocellulose, either through the mechanical homogenization of pulps to obtain Micro Fibrillated Cellulose (MFC), or through an acid hydrolysis procedure that results in crystalline cellulose nanowhiskers (nanoscale structures). Although originally considered for uses such as food and cosmetic additives, the potential of nanocellulose as a nontoxic and renewable polymer-reinforcing agent is now increasingly recognized. Novel applications for wood-derived nanomaterials, such as carbon nanotubes and cellulose nanofibers have already been developed (FPInnovations, 2013). Nanofibers and nanotubes are used in the textile industry to make tear-resistant and waterproof fabrics. These nanomaterials have been added to concrete in order to

increase its tensile strength and to halt the propagation of cracks. Other uses include solar cells and air filters. Thus these wood-derived nanomaterials can be used to enhance the durability and strength of products. The Forest Products Laboratory in the U.S. has been evaluating a new wood-derived nanomaterial that is composed of nanocrystals and nanofibers, in order to produce reinforced glass (Vinnitskaya, 2012). Cellulose fibers and plastic are currently being combined to produce Wood Plastic Composites (WPCs). Such products allow the use of recycled plastic bags and wood residues (UNECE/FAO, 2012).

In addition to ethanol and butanol, the various products from hemicelluloses in a biorefinery include barrier materials, hydrogels, fiber additives, and composites. Of these possibilities, the favorable oxygen-barrier properties of hemicellulose films are of considerable interest, and commercial applications in packaging are therefore being explored. Hydrogels based on hemicelluloses are said to have potential uses in the health care and pharmaceutical industries.

As well as its use for energy production, lignin from a wood biorefinery is one of the very few renewable sources for bulk aromatic chemicals, e.g. phenols and, as such, may be converted to commercial products, including adhesives, dispersants, and carbon fiber. The latter has good market-growth potential related to the strong, lightweight composite materials demanded by the automotive, aircraft, and aerospace industries; however the application areas can expand if carbon fiber becomes available relatively cheap. Lignin also has been used as an additive in thermoplastic composites, some of which are now in commercial applications as varied as loudspeakers, toys, and automotive parts.

Future shortages of the fossil hydrocarbons from which most organic chemicals are derived may result in the economic feasibility of the production of these chemicals from wood (Goldstein, 2012).Today, chemicals derived from wood include bark products, cellulose, cellulose esters, cellulose ethers, charcoal, dimethyl sulfoxide, ethyl alcohol, fatty acids, furfural, hemicellulose extracts, Kraft lignin, lignin sulfonates, pine oil, rayon, rosin, sugars, tall oil, turpentine, and vanillin.

3. THEORY

This section introduces wood as a raw material, particularly its structure at different size levels. The influence of wood morphology on the transport of materials in softwoods is discussed, as well as the different mass transport phenomena that occur during the impregnation of wood with chemicals are also discussed. A review of papers that deal with mass transport, especially diffusion in wood, is also presented.

3.1 Woody plants

In the evolutionary classification of plants, trees belong to the category of spermatophytes. There are two subdivisions of tree species namely, angiosperms and gymnosperms. Shrubs as well as trees of coniferales are included in the gymnosperms class. Conifers can be classified as trees with exposed seeds on the scales of cones, and coniferous trees are referred to as softwoods. The angiosperm subdivision is mainly split into eudicotyledons and monocotyledons, and includes leaf carrying trees, grasses and herbaceous plants. The woody plants in the angiosperm class are called hardwoods. Today more than 90% of the land plant species are angiosperms. Gymnosperms are trees such as pine (*Pines*), spruce (*Picea*), and fir (*Abies*), and typical angiosperms include the hardwoods birch (*Betula*), beech (*Fraxinus*), oak (*Quercus*), and poplar (*Populus*). The most common wood species industrially used in Sweden are spruce (*Picea abies*), pine (*Pinus sylvestris*), and birch (*Betula verrucosa*) (Henrikson et al., 2008).

3.2 Wood structure

Wood is a heterogeneous material. There are large variations in structure both between and within trees. Many studies on the structure of wood can be found in the literature (e.g. Fengel and Wegener, 1984; Sjöström, 1993; Miller, 1999; Rowell, 2005; Wiedenhoeft, 2010). An understanding of the nature of the various capillary components of wood and the extent to which each is effective in controlling the transport of liquids, dissolved materials, and chemicals through wood is of major importance. Wood is composed of different kinds of capillaries variable in size from structures observable to the naked eye down to capillaries that approach molecular dimensions. The way in which each of these capillary structures influences the transport of material differs not only with the structure but also with the nature of the driving force. Thus it is necessary to understand the nature of the driving force and its relationship to structure in order to determine the extent of the transport of materials through wood, and to determine the structure mainly responsible for controlling this transport (Stamm, 1946). In general softwoods have a more uniform structure with a fewer number of cell types than hardwoods. Another main difference between the two wood types is that hardwoods have special vessel elements for transporting water, while softwoods lack this cell type in their structure and the water transport occurs through tracheids (via lumen cavities/pits). However, this study focuses on Norway spruce, and therefore only softwood structural details are described in the text below.

3.3 Levels of wood structure

The fundamental structure of wood from the molecular to cellular or anatomical level determines the properties and behavior of wood. Four different levels of wood structure can be identified:

3.3.1 Macroscopic structure

When a tree stem is cut transversely, a surface appears that is composed of various annual growth rings present in concentric bands (See Figure 3.1). The tree consists of several layers from outside to inside: outer bark, inner bark, vascular cambium, sapwood, heartwood, and pith. Bark can be divided into an outer corky dead part, the thickness of which varies greatly with species and age of trees, and an inner (phloem) thin living part, which carries nutrients (sugars produced by photosynthesis) from the leaves to growing parts of the tree e.g. roots. The outer bark provides mechanical support and protection to the softer inner bark and also helps to limit evaporative water loss (Wiedenhoeft, 2010).The cambium layer which is inside the inner bark and forms wood and bark cells can be seen only with a microscope. Growth in the thickness of bark and wood is caused by cell division in the cambium. No growth in diameter takes place in wood outside the cambial zone; new growth is purely the addition and growth of new cells, not the further development of old ones. New wood cells are formed on the inside of the cambium and new bark cells on the outside. Thus, new wood is added to the outside of old wood and the diameter of the woody trunk increases.

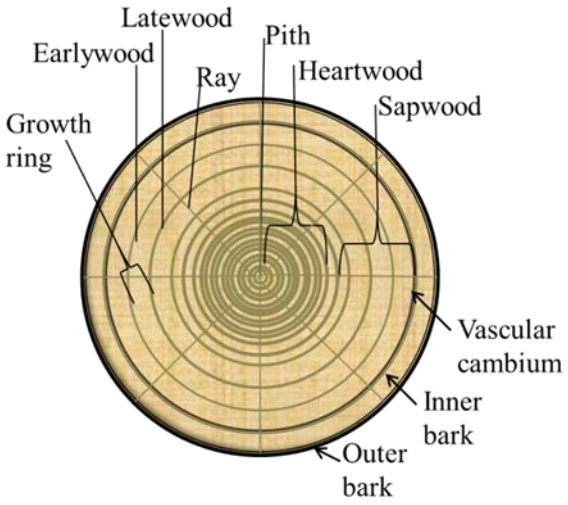

Figure 3.1 Macroscopic view of a transverse section of tree stem

Sapwood (Sw) is next to the cambium and contains both living and dead cells, and functions primarily in the storage of nutrients and mechanical support. The outer layers, near the cambium, handle the transport of water or sap. The Sw may vary in thickness and number of growth rings. In general, Hw consists of inactive cells that do not function in either water conduction or nutrients storage. The transition from Sw to Hw is accompanied by an increase in extractive

content. Frequently, these extractives darken the Hw. Hw has a lower moisture content than Sw does. Hw extractives may also affect wood by; (a) reducing permeability, and thus making the Hw slower to dry and more difficult to impregnate with chemical substances, (b) increasing stability in changing moisture conditions, and (c) increasing weight (slightly). However, as Sw changes to Hw, no cells are added or taken away. The basic strength of the wood is essentially not affected by the transition from Sw cells to Hw cells. The pith is a small core of tissue located at the center (inner layer) of a tree stem. This layer comprises remnants of the early growth of the tree stem before wood formation. In most species in temperate climates, the difference between wood that is formed early in a growing season and that formed later is sufficient to produce well-marked annual growth rings. The inner part of the growth ring formed first in the growing season is called earlywood and the outer part formed later in the growing season is called latewood (See Figure 3.1).

3.3.2 Microscopic structure

Softwoods consist mainly of longitudinal tracheids (90-95 % of cell volume) and a small number of ray cells (5-10 % of cell volume) (Fengel and Wegener, 1984; Brändström 2001).The longitudinal tracheids are herein, for the sake of simplicity, referred to as fibers. All fibers are hollow, elongated tubes, tapered and closed at both ends, and are something between rectangular and elliptical in a cross-section. The hollow void inside them is called the lumen, and enables water transport within the fibers. The distribution of fluids between adjacent cells is achieved through a system of pits, which allow intercellular communication. The average length of Scandinavian softwood (Norwegian spruce and Scots pine) fiber is 2-4 mm and the diameter is about 0.02-0.04 mm, but may range from 0.015 to 0.08 mm (Kazi, 1996). The tracheids are structured in fairly regular radial rows, and are extended parallel to the axial direction of the tree. Earlywood is characterized by cells with relatively large cavities and thin walls, and their main function is transport of water and nutrition. Latewood cells serve more as mechanical support, and these cells have smaller cavities, thicker walls, and longer length than earlywood. In Norway spruce the average content of latewood has been reported to be 20-25% on a volume basis. The transition from earlywood to latewood may be gradual or abrupt (See Figure 3.1), depending on the kind of wood and the growing conditions at the time it was formed. When growth rings are prominent, as in most softwoods, earlywood differs markedly from latewood in physical properties. Earlywood is lighter in weight, softer, and weaker than latewood. Because of the greater density of latewood, the proportion of latewood is sometimes used to judge the strength of the wood. (Brändström, 2001; Miller, 1999). Earlywood fibers have an average cell wall thickness of 2-4 μm and latewood fibers have an average cell wall thickness of 4-8 μm (Sjöström, 1993). The radial system is made up of ray cells, which run perpendicular to the fibers and across the void volume of the wood. These cells are known as wood rays (See Figure 3.1). Ray cells have an average length of 0.01-0.16 mm and a diameter of 2-50 μm. The main functions of wood rays are to redistribute and store nutrients, e.g. starch. Fibers (i.e. longitudinal tracheids) vary considerably in width in the radial direction, depending on the part of the growing season in which they were formed. A number of softwoods also contain vertical and horizontal resin ducts

(channels), but these are usually filled with resin. Their contribution to diffusion and flow is minor (Burr and Stamm, 1947). The other types of cells are parenchyma (ray canals) and epithelial cells (resin canals). The parenchyma cells are involved in the transport of liquids in the horizontal direction (Rowell, 2005).

3.3.3 Ultra structure

The cell wall of a mature cell in wood consists of different layers (See Figure 3.2 **A**): a thin outer layer called the Primary wall (P) and the thicker inner layer toward the cell cavity called the Secondary wall (S). The secondary wall consists of three sub layers: the transition layer or outer layer of the secondary wall (S_1), the central layer of the secondary wall (S_2), the tertiary wall or inner layer of secondary wall (S_3). Individual cells are connected together by the intercellular middle lamella region (ML). ML and P are formed first in the cambium, ML is very thin but becomes thicker later. Reasonable agreement exists as to the true structure of the individual layers as reflected by the numerous different models shown in the literature. Cell walls consist of long fibrils (0.1 to 5 µm) oriented at a slight angle (mostly in S_2) to the fiber axis and wrapped by a layer of other fibrils practically at right angles to them. Pits are the characteristic structures of wood that occur in the cell walls (Figure. 3.2 **B**). They represent canals that facilitate the transport of liquids both horizontally and vertically through the cell walls. Pits have a variety of shapes and sizes that together with their position on wood cells can be used as an investigative feature of wood classification.

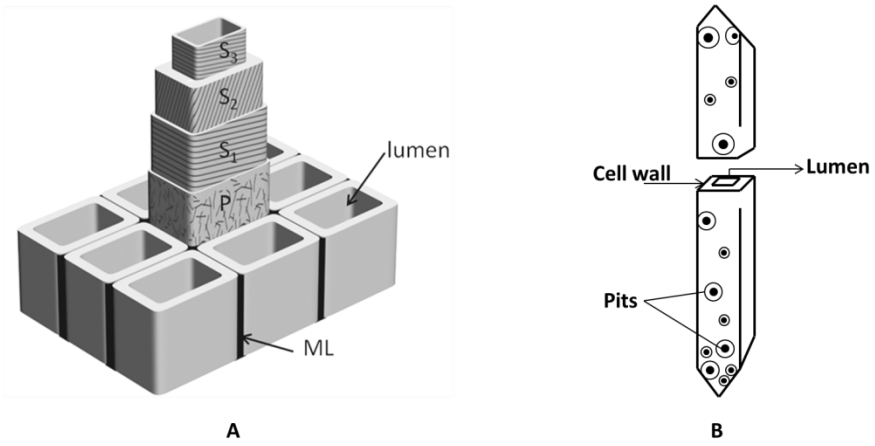

Figure 3.2 A. - The different layers in the cell wall of wood. ML: middle lamella, P: primary cell wall, S1, S2, S3: secondary walls, illustration from Saltberg, (2009). **B. -** Radial surface of softwood tracheid. Note the pits on the side walls and the 'lumen' inside of the hollow cell.

Pits of adjacent cells are normally paired by forming pit pairs. There are three common types of pit pairs: simple (link between parenchyma cells), bordered (in the radial walls of the tracheids and link tracheids to tracheids), and half-bordered (connect the verticals tracheids with horizontal ray parenchyma cells) (Figure 3.3). All pits have essentially two main components: a pit cavity and a pit membrane. The pit membrane consists of a primary wall and a middle lamella and since

the pits occur in pairs the membrane is composed of two primary walls and a middle lamella. Pits are exclusively localized on radial cell walls and are more at the ends of tracheids than in the middle parts. Since the main function of earlywood tracheids is to facilitate the major part of the transport of liquids, earlywood tracheids has abundant pits as compare with latewood tracheids; thus the impregnation of latewood is more difficult than impregnation of earlywood. There are approximately 50 to 300 pits per tracheid in earlywood and 10 to 50 in latewood (Stamm, 1946). The pit membranes of bordered pit pairs have a central thickened portion, called the torus (T), which is often pushed against the cell wall opening and possibly sealed in this position with resinous material thus their effectiveness in transporting materials is largely reduced. Such pits are known as aspirated pits.

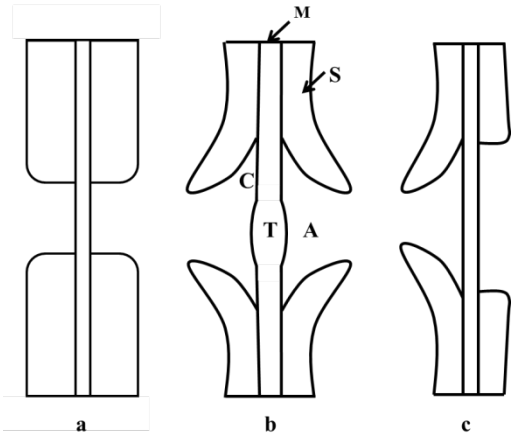

Figure 3.3. Three basic types of pit pairs. **a** simple pit pair; **b** bordered pit pair; **c** half-bordered pit pair. **A** aperture; **C** chamber; **M** middle lamella-primary wall; **S** secondary wall; **T** torus

The bordered pits on the tangential walls of longitudinal tracheids are always smaller than those on the radial walls (Kazi, 1996). The pit chamber is roughly in the form of a truncated cone, the smaller end opening into the fiber cavity and the larger end closed by the pit membrane. The pit membrane is three to four times as large in diameter as the pit opening.

3.3.4 Molecular structure

Wood has an elemental composition of about 50% carbon (C), 6% hydrogen (H), 44% oxygen (O), and trace amounts of several metal ions (Pettersen, 1984). The three major elemental compounds (C, H, and O) are combined in complex molecules that are then joined into polymers. These polymers provide the structural integrity of wood. In addition, wood contains small quantities of other organic and inorganic compounds. The polymers of wood can be classified into three major types: cellulose (composed of β-D-Glucopyranose units linked together by (1→4)-glycosidic bonds), hemicelluloses (mixtures of simple sugars and sugar acids that are synthesized in wood from glucose, mannose, galactose, xylose, arabinose, 4-O-methylglucoronic acid, and galacturonic acid residues), and lignin (contains methoxyl, phenolic hydroxyl, and some terminal aldehyde groups) (Sjöström, 1993). The proportion of the three polymers varies between species. A typical composition of softwoods is: cellulose which comprises 40-50% of the weight

of extractive free wood; hemicelluloses which comprise 20-30%; and lignin which comprises 20-30% of the weight of the extractive-free wood (Kazi, 1996). There are many other chemical compounds in wood. They usually make up only a few percent of the total composition of wood, but in some cases can be considerably more. In most cases these compounds are not an essential part of the structure of wood. One class of compounds is called extractives, and represents a wide range of classes of compounds. These components include both water-soluble and organic-soluble extractives, on an average up to 10% in softwood such as red pine. One group of extractives that is important commercially is the oleoresins, from which turpentine, rosin and various other oils are derived. Another group of extractives are polyphenols, which include tannins, flavones, kinos, and lignans. Other organic compounds include gums, tropolones, fats, fatty acids, and waxes. There are also inorganic compounds in wood. They are generally called ash as a group. Metal ions such as: calcium, potassium, magnesium, manganese, and silicon are common elements in wood (Saltberg, 2009). Under neutral or weakly acidic conditions, wood components with acidic groups such as carboxylic groups contribute to the ion exchange capacity of the wood material. However, phenolic hydroxyl groups, and the very weak alcoholic groups are ionized only in the presence of strong alkaline conditions. Carboxylic groups in wood, such as 4-O-methyl-glucuronic acid in xylan and galacturonic acid in pectic material, are primarily involved in ion exchange equilibrium reactions (Sjöström, 1993).

3.4 Shrinking and swelling of wood structure

Moisture in wood is found in two forms: as liquid water in cell walls and as liquid and/or vapor in cell cavities. Water held in cell walls is called ‘bound water’ and that which is held in cavities is called ‘free water’. The condition at which the cell walls are saturated with bound water but with no free water in the cavities is called the fiber saturation point (Saiu, 1984). At saturated conditions, only liquid water is bound in the cell walls. The basic reason for moisture entering into the mass of wood is the attraction of water molecules by the hydroxyl groups of chemical constituents of wood, mainly cellulose (Kazi, 1996). As a result, a mono-molecular layer of water is found which interacts with hydroxyl groups via hydrogen bonds. The formation of this layer results in chains of cellulose molecules being pushed apart in the amorphous regions and between the crystallites of the microfibrils so that wood starts to swell. Under the effect of secondary attractive forces (Intramolecular hydrogen bonding), more water molecules enter and form a poly-molecular layer. An additional part may enter by capillary condensation in cell wall voids and pit features such as pit membrane openings and small pit mouths. After the saturation of cell walls, liquid water may also enter cell cavities.

The hydroscopic swelling and shrinking in wood occurs as a result of changes in the moisture content (Saiu, 1984). In green (living) wood the fibers are always swollen. When the wood is cut, the moisture content in the wood structure may decrease. When the moisture content is reduced below the fiber saturation point, the fibers shrink. This shrinking causes the cracking in the fiber walls that affects the diffusion as an increased number of paths, and/or smaller lumen are developed. In most cases, wood pieces used in diffusion measurements have moisture content

higher than the fiber saturation point which thus leads to tangential swelling. The swelling can easily be seen as an increase in volume (Skaar, 1972), and the longitudinal swelling is much smaller than the transversal swelling. Some electrolytes increase the swelling by softening the cell walls (Wallström and Lindberg, 2000). These solutions usually have a very high pH, e.g. NaOH and white liquor. This phenomenon may occur because the solution can penetrate the wood from the lumen through the secondary wall layer S_3 into the middle lamella. This allows the fibers to swell outward in as well as inward.

3.5 Structure through which transport of materials occurs in softwoods

It is essential to know the dimensions and structure of the different capillary structural components for a deeper understanding of the transport of materials through softwoods (Stamm, 1946). The diffusion rate is directly dependent on the structural dimensions and the chemical composition of the inner walls of a fiber (Saiu, 1984). Although some of these wood properties vary, although slightly, from species to species, other properties may vary considerably. The transport of fluids through softwoods is essentially through the tracheids which are interconnected by bordered pit pairs. A schematic illustration of a simplified fiber matrix is given in Fig. 3.4. This figure shows schematically the diffusion path in the longitudinal and transversal directions. The real case of diffusion through wood is more complex since there are blocked pores, a variety of different fiber and pit sizes, pit pair types, and capillary pore types, along with the overlap of the tracheid cells.

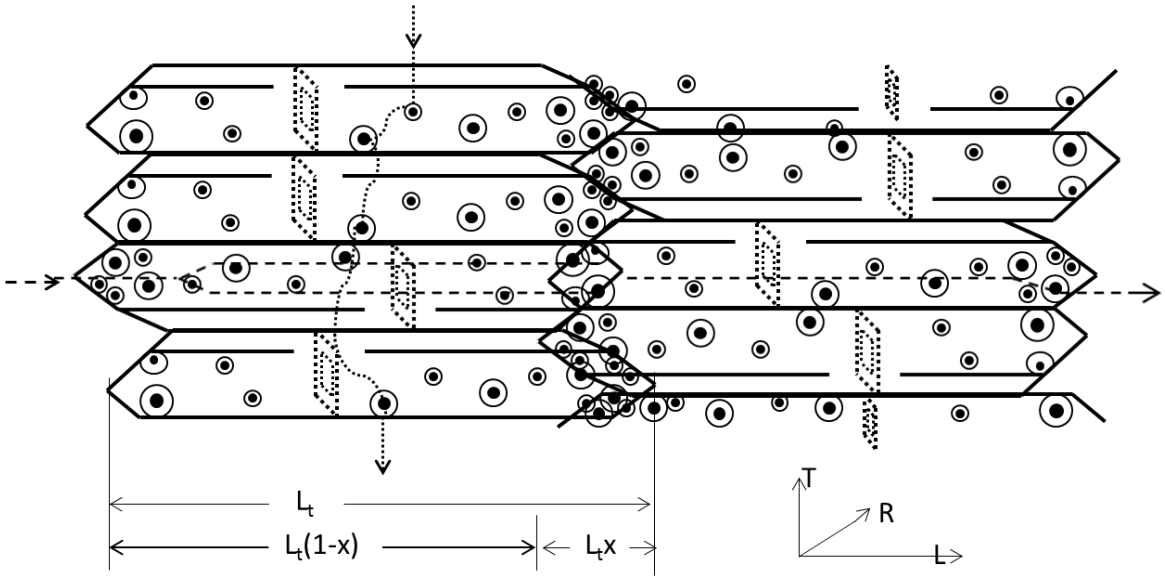

Figure 3.4. Simplified illustration of a swollen tangential section of softwood, showing the complex series and parallel combinations of fiber cavities, pit chambers, pit-membrane pores, and transient cell-wall capillaries. The tangential section shows most of the pits on the radial surfaces of the tapered ends of the tracheids. L_t = length of tracheid; x = fraction of tracheids overlap.

The transport of a material through wood in any of the three major structural directions may occur through a fiber cavity, into a pit chamber, through a permanent or transient pore in the pit membrane and into the next pit chamber and fiber cavity; through a fiber cavity and through the swollen cell wall into the next fiber cavity; or continuously through the cell wall capillaries (Burr and Stamm, 1947). The transport of fluid through wood samples is thus complicated because of the complex capillary system of wood. The liquid transportation mechanism through capillaries depends on the characteristics of the transportation path which eventually depends on the dimension of the pores. For small wood pieces, with a length in fiber direction shorter than the tracheid length, most capillaries are cut once across leading to a high effective capillary cross-sectional area. In contrast, big wood pieces, with a length in fiber direction longer than the maximum tracheid length, do not have an open-ended capillary tube, and chemical transportation through the capillaries is controlled by the bordered pits covered by the pit membrane with a thickness of around 1 micron (μ) (Kazi, 1996). The Effective Capillary Cross-Sectional Area (ECCSA) is different in the three structural directions of wood and increases in the following order: tangential, radial, and longitudinal, which stems from the different values of the diffusivity constants in these three directions (Stone, 1957). The diffusion rate of chemicals into these directions can be related to the capillary cross-sectional area. Because of the fact that the radial and tangential directions cover the cell walls alone, capillary pores in these directions are rather small compared to the longitudinal direction. Therefore, the diffusivity in the radial and tangential directions is nearly equal under all conditions (Talton and Cornell, 1987). There seems to be a slight tendency for the maximum effective pore diameters to decrease with an increase in the thickness of the wood pieces (Kazi, 1996). The diffusion of dissolved materials in the fiber direction (longitudinal) is a direct function of the void volume of the wood, and is less dependent on pit structure, but the transverse diffusion is highly dependent on both the structure of pits and the various other sizes of capillaries (Stamm, 1946).

3.6 Impregnation of wood with chemicals

Impregnation is a method commonly used in the treatment of wood materials with different varieties of chemicals or resins in order to improve wood properties such as dimension stability, chemical and biological resistance, weathering and mechanical properties, and fire resistance (Kazi, 1996). Impregnation is also the first step in conventional pulping or in wood conversion processes, followed by cooking, steam explosion or any other process. Thus, in many cases, chemicals must be transported into wood prior to a reaction, and consequently the wood material has to be impregnated with the reactants.

During impregnation, chemicals are transferred into the core of the wood by two primary mechanisms which are entirely different. (Stone and Förderreuther, 1956). The first mechanism, liquor penetration, refers to the flow of liquor into the gas/steam-filled voids of the wood material, under the influence of the pressure gradient. The second mechanism, diffusion, refers to the movement of ions or other soluble matter through liquid inside the wood material, under the influence of the concentration gradient. In fresh wood, both mechanisms occur at the same time,

but in certain cases, e.g. Kraft cooking most of the chemicals are transported into wood by diffusion. The role of penetration is to fill fiber cavities with liquid, which enables a faster and more even diffusion of chemical ions into the wood (Määttänen and Tikka, 2012).Penetration occurs very fast in the beginning if there are any gas/steam-filled pores, but diffusion is the mechanism involved if the pores are completely filled with liquid, and is much slower. Proper impregnation of wood with chemicals is of great importance for economically viable and efficient chemical pulping, as well as biorefinery processes, since homogeneous impregnation increases the uniformity of the treatments and reduces reaction times. Thus, a thorough understanding of the complex chemical transport phenomena of reactants into the wood matrix is critical and is therefore crucial for the success of biorefinery concepts.

In the conventional pulping process, a major portion of the required cooking chemicals (white liquor) is added at the beginning of the process. And the wood material contains water in the form of moisture from the beginning of the pulping process, and that contributes to the dilution of the penetrated cooking liquor in the interior of the wood chips. Thus a concentration gradient (the driving force for diffusion mechanism) is also established between the bulk of the cooking liquor surrounding the wood chips and the liquor inside the fiber lumina. At later stages, as the temperature rises, the distribution of chemicals within wood chips occurs mainly by diffusion. This is due to the fact that the chemicals in the cooking liquor transported into the wood matrix by penetration are consumed in various reactions with lignin and polysaccharides, e.g. the neutralization of acidic groups present in wood or produced by the peeling of polysaccharides, and thus the concentration of penetrating liquor decreases rapidly. Therefore a concentration gradient is established between the bulk of cooking liquor surrounding the wood chips, fiber wall, and also the liquor inside the fiber lumina. During the earliest stage of alkaline pulping, the delignification curve is predicted well by unsteady-state diffusion theory (Gustafson, 1988). A large increase in mass transport rate of lignin with temperature is explained by an increase in cell wall permeability with temperature and the possible reduction in lignin molecular weight at higher pulping temperature.

In chemical pulping, it is important that cooking chemicals are present in all parts of the wood tissue where delignification (lignin is dissolved from wood tissue in order to separate fibers from the wood matrix) takes place before cooking temperature is reached, otherwise the quality of the produced pulp will suffer. A considerable proportion of the numerous investigations concerned with the penetration and diffusion phenomenon into wood have studied the influence of different experiemntal conditions such as temperature, pressure, pH, the viscosity of the solution. In many cases, these investigations have been conducted with gases, pure water, or liquids and solutions that are not used in pulping. However, the importance of thorough liquor impregnation prior to cooking is widely recognized in the pulping industry. Poor impregnation of cooking chemicals is reflected in the form of decreased uniformity of pulping (Bengtsson and Simonson, 1984; Gustafson et al., 1989; Gullichsen et al., 1992; Malkov et al., 2003) and higher amounts of rejects in the final pulp. Bengtsson and Simonson (1984) have found that poorly impregnated chips

contain a significant amount of less treated wood which can produce a pulp composed of a large portion of stiff, shortened fibers that form weak interfiber bonds. Stone and Green (1959) have observed that incomplete impregnation, and thereby the resulting non-uniform pulping, produces higher shieves and screenings in the final pulp, a higher lignin content at a given yield, and an inferior bleachability and end use properties. On the other hand, complete impregnation reduces cooking time, increases pulp uniformity and prevents undesirable lignin reactions. Gustafson et al., (1989) have studied the relative effect of diffusion and penetration on Kraft pulping uniformity and the effect of chip thickness and liquor to wood ratio on pulping behavior, with particular emphasis on the relative importance of diffusion and capillary penetration. Their findings show that a significant portion of chip sizes found in commercial digesters fall into the diffusion-controlled category.

3.7 Diffusion in wood

Diffusion is a phenomenon involving the movement of one material into another from a zone of higher concentration to a zone of lower concentration (Stamm, 1967; Siau, 1984). The basic mechanism of diffusion is random molecular motion. Diffusion in its simplest form, that is uni-dimensional diffusion, can be expressed using Fick's first law of diffusion:

$$\frac{dM}{dt} = -D\,Az\,\frac{dC}{dz} \qquad (3.1)$$

Where, mass change per unit time, $^{dM}/_{dt}$ is proportional to the concentration change per unit distance (z) in the diffusion direction, $^{dc}/_{dz}$ per increment of area A_z.

When two different fixed concentrations are maintained at the two end surfaces of a thin plate of a porous, inert body, a constant concentration gradient is eventually set up across the plate. When the steady-state concentration condition is attained, the rate of diffusion through the plate is constant, M/t, and can be expressed in its integral form of Equation (3.1),

$$\frac{M}{t} = \frac{D\,Az}{S}(C1 - C2) \qquad (3.2)$$

In which, A is the effective area, and S is the thickness of the material through which diffusion occurs, and $(C1 - C2)$ is the concentration difference.

However, diffusion into or from a porous material, such as wood, is much more complicated, e.g. pulp cooking conditions, than diffusion under steady state conditions through a porous, inert material. The boundary conditions, for example, continuously change. During the impregnation of chemicals into wood, the wood material becomes swollen to different degrees. In alkaline solutions, the wood structure changes due to swelling. The reactions with various wood components also consumes alkali, and organic matter dissolves, which in turn affects the mass transport rate due to increased cell wall permeability (Gustafson, 1988). Thus, for a given agent concentration in solution, e.g. NaOH, the swollen wood matrix can be considered as having an

invariant geometry with time. Additionally, the interaction between wood and the migrating ions affects the mass transport rate. A solute migrates faster through an open area (lumen) than through a partially-closed area (pit or pit membrane). If the solute sorbs at the cell wall, it may migrate differently than in the bulk liquid. Thus diffusion is affected by both physical and chemical conditions. Therefore, under these dynamic conditions the diffusion process can be expressed using Fick's second law of diffusion,

$$\frac{\partial C}{\partial t} = -\frac{\partial}{\partial z}\left(D\frac{\partial C}{\partial z}\right) \qquad (3.3)$$

In which, the change in concentration over time, $\frac{dC}{dt}$ at any point in the z direction of the porous material is proportional to the rate at which concentration varies over distance, that is the second derivative of concentration with respect to distance, $\frac{d^2C}{dz^2}$. There is no single simple integral solution of this differential equation, but various solutions have been derived depending on the initial, boundary, and other conditions together with whether or not the diffusion coefficient D varies with concentration C (Crank, 1970).

The diffusion coefficient, D, increases with increasing temperature. An Arrhenius type of equation is commonly used to describe the temperature dependence of the diffusion coefficient (Robertsen, 1993):

$$D = A_f T^{1/2} e^{(-E/RT)} \qquad (3.4)$$

Where D = diffusion coefficient, A_f = frequency factor or pre-exponential factor, T = absolute temperature, E = activation energy and R = general gas constant.

3.7.1 Factors limiting the diffusion of ions in wood

The diffusion of ions in wood has been studied for different purposes, e.g. the diffusion of ions under pulping conditions (Robertsen, 1993; Bengtsson et al., 1988; Sharareh et al., 1995), and in wood preservative treatment (Vinden, 1984; Cooper, 1998).

Important factors that limit the diffusion of ions in wood are:

- **Wood properties**: Different wood types (within the tree: Sw vs. Hw; juvenile vs. mature wood; reaction vs. compression wood; and among different wood species) have different capillary structures, which therefore affects the diffusion paths inside the wood. This affects the rate of diffusion through the wood, at least in the early stage of impregnation, where the permeability of wood remains unchanged. Törnqvist et al., (2001b) have found significant difference in diffusion in different wood species. Birch had a significantly higher diffusion coefficient in the transversal (radial) direction than spruce and pine due to different capillary structures, but the differences were negligible in the longitudinal direction. The grain orientation also influences the rate of diffusion, and the rate of

diffusion in different directions in wood generally follows: longitudinal >> radial > tangential.

The general concept is that the diffusion of chemicals into the center of the wood chip is the limiting factor in pulping. Since the diffusion rate is relatively equal in all directions within the chip under strong alkaline conditions (pH >13) inside the wood chips which occur after some cooking time, most of the chemicals needed during that phase of pulping will be transported in the direction of the shortest chip dimension, i.e. chip thickness. Because chip thickness is the shortest path between the edge of the chip and the center of the chip; it controls the level of delignification at the center of the chip. Therefore, at high pH inside the wood chip, chip's thickness is an important measurement of chip quality because of the limitation of chemical diffusion within the chip (Akhtaruzzaman and Virkola, 1979). The total void volume of water in swollen wood can be divided into permanent capillaries, as lumen and in the cell wall, and transient capillaries in the cell wall. These transient capillaries exist only when the wood is swollen and they are very small, but nevertheless important for the diffusion process (Kazi et al., 1997).

- **Degree of saturation**: it is generally true that higher moisture content facilitates diffusion. Diffusion is a complex process when the water is not continuous throughout the wood matrix. In un-saturated wood pieces, localized barriers to diffusion are created by zones of gas or vapor that breaks up the water pahse. This leads to a decrease in the number of pathways available for diffusion. The diffusion rate is at its maximum when the pore structure of a wood piece is saturated with water. Thus the diffusion rate varies depending on the uniformity of the water throughout the wood matrix.
- **Temperature**: the diffusion rate generally increases with an increase in temperature, since temperature affects the mobility of ions, thus diffusion, and subsequently the diffusion coefficient.
- **Properties of chemical solution:** Concentration gradients are the main diffusion driving force: the diffusion of chemicals into wood can be controlled to some extent by the concentration of the impregnation solution. Important factors that affect the mass transport rate of chemicals into wood, related to the properties of chemical solution, are sorption, temperature, pH, concentration, surface tension and viscosity (Stone and Förderreuther, 1956).

3.8 Measurement of diffusion of chemicals into wood

3.8.1 Available methods for measuring diffusion of chemicals into wood

There are currently several methods described in the literature for measuring liquid phase diffusion into wood, but no standard method exits. A review of the literature has shown that the first PhD thesis on molecular diffusion into wood was submitted in 1934 (Cady and Williams, 1935). This work was inspired by the diffusion experiments across the interface between a moving liquid and a gel in a stirring bath, but was extended to conditions valid for wood. These

authors studied the diffusion of urea, glycerol and lactose into several water-saturated softwoods relative to their diffusion in water. In 1947, another PhD thesis was published with title 'Diffusion in Wood' (Burr and Stamm, 1947). During 1941 to 1947, most of the research was related to developing the theoretical expression for the rates of transport of vapors, liquids, and dissolved materials through softwoods in the three structural directions under various conditions of temperature and moisture content (Stamm, 1946; Burr and Stamm, 1947). In the beginning of the 1950´s, the diffusion of salts, ion and organic molecules through some green timbers was extensively studied (Christensen and Williams, 1951; Christensen, 1951a & b; Narayanamurti and Ratra, 1951; Narayanamurti and Kumar, 1953; Behr et al., 1953). A quantitative theory on diffusion in wood was provided by Christensen and Williams (1951). The effect of wood structure on diffusion was widely studied using the electrical conductivity measurement of the impregnated wood block. These measurements were compared with the electrical conductivity of the chemical solution. The ratio of the two conductivities was considered as a direct measurement of effective capillary cross-sectional area (ECCSA). ECCSA is the cross-sectional area of the paths available for diffusion. Stone and Green (1959) used this method to study the effect of pH on the diffusion of KCl in the three structural directions of aspen wood species. They found that up to a pH of 12, the ECCSA in the longitudinal direction is approximately 5 times greater than the ECCSA in the transverse and radial directions. But at a pH above 13, the ECCSAs in all three directions are about the same because of fiber swelling. The ECCSA is a measurement of wood structure and it can be used to compare wood directions or to rank wood species.

Later in the 1980`s, most of the research was directed towards measurements of the diffusion of nonelectrolytes (monohydric alcohols, polyethylene glycols) through wood (stika spruce heartwood) saturated with water with a highly sensitive differential refractometer (Fukuyama and Urakami, 1980, 1982, 1986). These studies emphasized the variation of the diffusion coefficient associated with wood structure. Much attention has also been given to the diffusion of bound water through the cell wall (Siau, 1984; Skaar and Siau, 1981). These studies have mainly proposed empirical equations to represent the effect of temperature and moisture content on bound-water diffusion in the transverse direction of wood. Tracer techniques using radioactive isotopes have been used to evaluate the impregnation of pulping chemicals during chemical and chemimechanical pulping (Bengtsson and Simonson 1984). After impregnation, the samples were sliced and the beta activity from the whole surface of slice was used as an indication of the degree of diffusion. The effect of transient acid diffusion in fully saturated aspen wood chips on the hydrolysis of hemicelluloses has been studied by Tillman, et al. (1990). These researchers developed a theoretical model in order to investigate the effects of nonuniform acid diffusion during hemicellulose hydrolysis.

One of the frequently used techniques employed to measure the diffusion of solute ion into water saturated wood is based on the rate at which ion diffuse through a wood slice whose sides are in contact with solution of different concentrations or in a water bath in which a completely impregnated wood block has been placed. Robertsen, (1993) used this technique to study the

effects of concentration and temperature on the diffusion of NaOH in the radial direction of spruce. One of the limitations of this method is that it gives an average diffusivity and cannot differentiate between areas of differing diffusivity within a wood specimen. The Scanning Electron Microscopy/Energy Dispersive X-ray Analysis (SEM/EDXA) method was developed to measure liquor diffusion by measuring the concentration of a chemical at a defined area in the wood chip (Bengtsson et al., 1988; Sharareh et al., 1996). The advantage of this method is that it is able to qualitatively as well as quantitatively show the profile of the ion in the wood chip as the ion is transported from the edge of the wood chip towards the center. Sharareh et al., (1996) have used this method to simultaneously measure the sulphur concentration in three structural directions of an impregnated wood chip. However, this method cannot differentiate between bound and free sulphur. In order to study the effect of the diffusion mechanism on the alcohol-based organosolv pulping process, unsteady-state diffusion experiments on methanol in Douglas-fir heartwood were conducted at high temperatures (Meijer et al., 1996). Results from this research indicated that the diffusion mechanism was the same as the one for alkaline solution diffusion in Kraft pulping and also observed a deviation in Fick's second law at low methanol concentrations. During the same period of time, a diffusion model for the impregnation of lignocellulosic materials was developed to ensure a uniform chemical distribution within the lignocellulosic matrix prior to rapid steam treatment (Kazi et al., 1997; Kazi et al., 1998). During their impregnation experiments with NaOH, these authors also observed that a large fraction of the inorganics, e.g. ash present in the lignocellulosic material (Straw) could be removed and thereby the quality of the fiber was improved, i.e. pure cellulose was produced. A new approach called 'Drift speed' was proposed in order to study the diffusion of ions into wood (Törnqvist et al., 2001a). This research has only focused on the effects of possible swelling during the transport of ions into the wood and this phenomenon is only dependent on the diffusion length and not on the active area available for diffusion.

In order to improve a number of wood properties, such as surface hardness and weathering resistance, some researchers have used the UV-microscopy to investigate the resin diffusion into softwood cell walls (Gindl et al., 2002; Gindl et al., 2003). Results from this research have demonstrated that UV-microscopy is a suitable technique to address the question of possible chemical transport into wood cell walls. A lot of research in the field of wood preservation has been conducted in order to understand the diffusion mechanism in wood cell walls. Some researchers have extensively studied the effect of various factors such as temperature, moisture content and pH on the diffusion of wood preservatives such as boron and copper into pine wood species (Cooper, 1998; Ra et al., 2001). Fourier Transform Near-Infrared Transmission spectroscopy (FT-NIR) has been applied to monitor the diffusion of deuterium-labeled molecules in Beech wood species (Tsuchikawa and Siesler, 2003). Some of the important conclusions from this research include: independent of wood species, the diffusion of the penetrant into the amorphous region was faster than that into the semi-crystalline region and the size effect of the diffusants (^{o}A) plays an important role for the diffusion process in wood. Recently, tritiated water, which is a conservative tracer for water, was used to understand the mass transfer

phenomenon in water-saturated wood particles of pine and aspen wood species (Jacobson and Banerjee, 2006). In that study the authors calculated the diffusion coefficient as a function of tortuosity, porosity, and the self-diffusion coefficient. From their research they concluded that mass transfer in wood was more than a simple Fickian mechanism and introduced the concepts of size exclusion and charge exclusion. However, this method must be tested for different chemical species as well as different wood species, and the effect of their structure, in order to gain broader knowledge. A model that describes the leaching of calcium ions from softwood chips, and takes into account cracks, rough surfaces and the size distribution of the wood chips, has been developed (Saltberg et al., 2006). Leaching experiments with hand-sawn pieces of spruce wood were conducted to determine the diffusion coefficient for calcium. However, this method cannot differentiate the concentration profiles at various positions within a single wood piece; the method just calculates the effective diffusion coefficient, and the natural content of calcium ions (softwoods- 600 to 1200 mg/kg wood) aggravates the measurements.

3.8.2 Drawbacks associated with the available methods

From this literature review it is clear that most of the investigations on chemical transport measurements of metal ions into wood pieces were based on either the average flux measurement of the diffusing substance or based on electrical conductivity measurements of an impregnated wood chip. These experimental results based on the electrochemical potential gradient were used to model the diffusion mechanism by using Fick's law. These methods have a limitation, e.g. the methods cannot be used to determine the concentration profile at various locations separately for each of the three different directions of a wood piece. Moreover, there are many aspects of diffusion of components into wood that have not yet been extensively studied. For example, most of the research on cation diffusion measurements into wood has been conducted using substances such as NaCl (sodium chloride), KCl (potassium chloride), and NaOH (sodium hydroxide). If NaCl/KCl is used as the diffusing substance, there is a possibility of inaccuracy in determining the cation diffusion into wood due to the original presence of Na^+/ K^+ ions as alkali metal ions in the wood. In the case of NaOH, the reactions of OH^- ions with wood components influence the pure diffusional effects of Na^+ ions. Furthermore, in most of the methods, after the completion of the impregnation time, the impregnated samples were either immediately processed further in the diffusion measurement procedures or were stored in a refrigerator at freezing temperature to stop any further diffusion. These slow freezing rates can lead to incorrect measurements. To minimize this effect, the impregnated wood pieces can be placed in liquid nitrogen (-180^{o}C), which has a very rapid freezing rate. Due to the rapid freezing rate, the effect of inward migration of chemicals/ions in impregnated wood samples can be minimized. Additionally, there are some observations that clearly indicate that almost all wood pieces have micro-cracks, which may be too small for direct visual detection, but these micro-cracks can change the capillarity of the surface layer and thus influence its interaction with surrounding liquor and/or also re-open the aspirated pits, thus making the layer a more open structure. These micro-cracks are due to a damaged surface layer as a result of the mechanical preparation of wood pieces, e.g. sawing

(Salin, 2008). These differences influence the behavior of a wood piece in diffusion measurements.

In order to overcome some of the difficulties stated above, in this study LiCl (Lithium Chloride) was chosen as the diffusing substance and we used a direct method of slicing the wood piece and measuring the Li^+ ion concentration with Flame Atomic Emission Spectroscopy (FAES). Even though wood contains very small amounts of naturally occurring Li^+ and Cl^- ions, the effect of the original presence of these ions on the cation diffusion into wood can be considered as negligibly small. Furthermore, Su et al. (2012) have demonstrated that Li^+ has low affinity towards wood components.

4. RESEARCH OBJECTIVES

Impregnation of wood with chemicals is of great importance in biomass conversion processes because a homogeneous impregnation increases the uniformity of the treatments and reduces reaction times. Additionally, efficient impregnation of the wood pieces ensures a uniform distribution of the moisture and chemicals within the pieces at the beginning of the reaction. Moreover, a thorough understanding of the key concept that takes place during the chemical transport of reactants into the wood matrix is critical and must be understood better for the success of any wood treatment process. Therefore, the main focus of this research is on developing an experimental technique that can:

i. differentiate between zones of different accessibility to chemical ions within a single wood piece.

ii. be used on samples of a wide range of shapes and dimensions and allow the concentration at any position in the impregnated wood piece to be measured.

iii. measure the concentration profile as a function of wood piece dimensions, impregnation time, temperature, and wood structure.

iv. gives a three-dimensional representation of the chemical concentration within a single wood piece.

v. operates under non-isothermal and unsteady-state conditions.

5. MATERIALS AND METHODS

5.1 Samples

In this study a stemwood disc with a diameter of 23 cm (without bark) of a 31±1 – year-old Norway spruce (*Picea abies* L) was investigated. Since wood can generally be regarded as an anisotropic, heterogeneous and hygroscopic material, numerous interacting factors have to be considered to investigate its material properties. Therefore a stem wood sample was divided into several types of tissues (Figure 5.1).

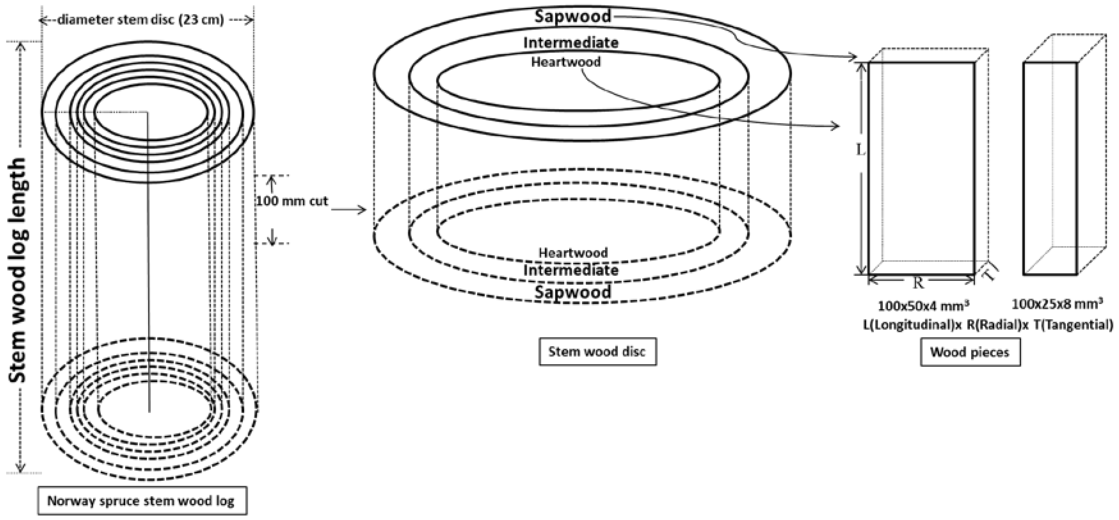

Figure 5.1 Preparation of rectangular prototype Sw and Hw pieces from Norway spruce stem wood log via stem wood disc; Description of the different flow directions used in the diffusion measurement tests (LxRxT).

Both Sapwood (Sw) and Hw (Heartwood) samples were carefully prepared using a vertical band saw machine (Mossner Rekord, August Mössner KG, D-7075 MUTLANGEN; metal cutting band saw: L.S. Starrett Company LTD. Jedburgh, SCOTLAND with 14 teeth per inch) and were kept in an airtight polyethylene (PE) bag at 1^{o}C to prevent decay formation. It was assumed that a stemwood disc contains 50% Sw, 30% Hw, and the remaining 20% is an intermediate between Sw and Hw (Sandberg and Sterley, 2009). Only Sw and Hw were investigated and not the intermediate material. Only rot- and other deformation-free samples were selected and cut into rectangular prototype pieces using the same vertical band saw machine as mentioned above. Two different dimensions were selected: 100x25x8 and 100x50x4 mm^3 (Longitudinal (L) x Radial (R) x Tangential (T)). The material was then stored in an airtight PE bag in a freezer at -18^{o}C to prevent moisture loss from the wood pieces. Defrosting the wood pieces took 24 h. Figure 5.2 illustrates the steps in the experimental procedure followed in the preliminary study. In order to minimize the surface damage to the wood pieces caused by the rough sawing procedure, the wood pieces were carefully planed on all 4 vertical surfaces to peel off surface layers from the

wood pieces at about 0.5 to 1.5 mm thick using a hand plane (Stanley Hand Tools, Stanley Canada, Mississauga, On L5N 7K6).

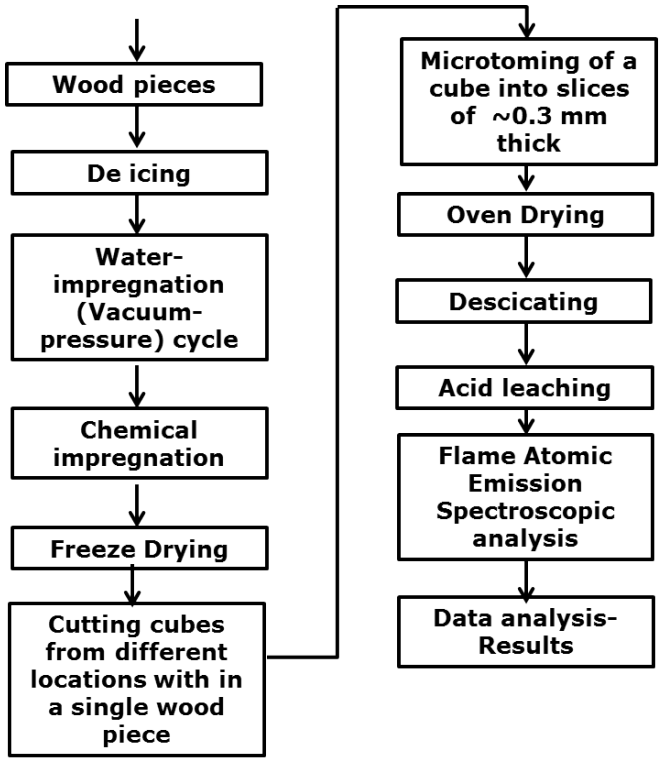

Figure 5.2 Step-wise experimental procedure of this study.

5.2 Water Impregnation Cycles

In order to limit the transport mechanism to the diffusion phenomenon, the wood pieces were water impregnated in a vacuum-pressure cycle. This was performed in a small polypropylene (PP) beaker placed in an autoclave filled with deionized water at ~ 22^{o}C, i.e. at Room Temperature (R.T.). First a vacuum was applied for 30 min and then the autoclave was pressurized with N_2 at 0.5 MPa for 1 h. This procedure was repeated until no floating pieces were observed after complete water impregnation (maximum 3-5 cycles for Sw and 5-15 cycles for Hw were needed). To eliminate the small bubbles left on the surfaces (possible barriers against chemical diffusion); the pieces were kept in the final vacuum for 30 min before the subsequent experimental steps. Subsequent experimental steps were completed shortly thereafter to minimize moisture loss from the wood pieces.

5.3 Chemical impregnation experiments: Impregnation with LiCl

The pieces were dabbed with filter paper and immersed in a solution of 1 M LiCl (Merck KGaA, Darmstadt, Germany) at a wood to liquor ratio of 1:50 during the preliminary study i.e. experiments at room temperature and 1:125 for the rest of the experiments (Figure 5.3).

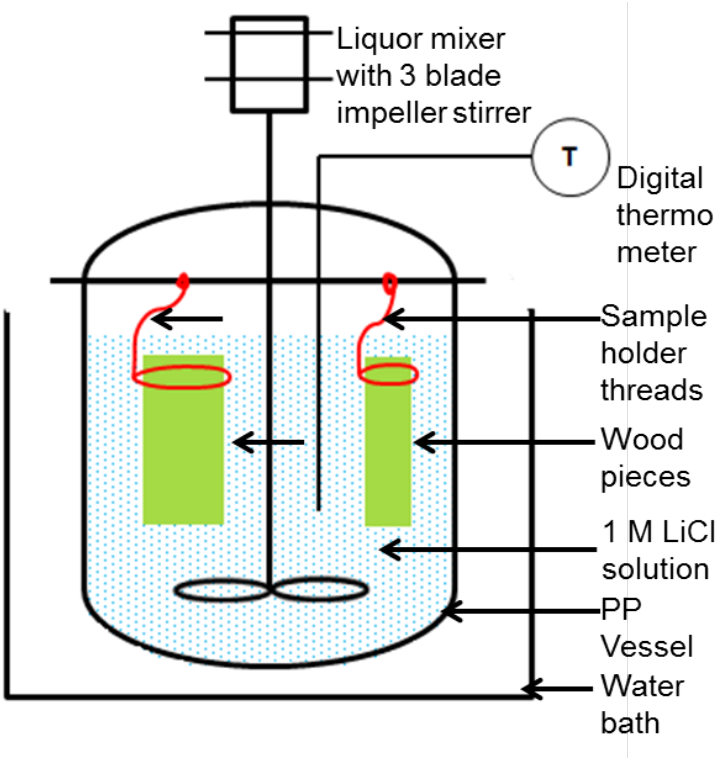

Figure 5.3 Experimental setup for impregnation with LiCl solution at different temperatures.

The impregnation vessel was made of PP and placed in an unstirred water bath (Sub Aqua 26 Plus, Grant Scientific, Grant Instruments (Cambridge) Ltd, SG8 6GB, England). The impregnation vessel was equipped with a liquor mixer fitted with a 3-blade impeller to avoid concentration gradients in the impregnation vessel, and with a digital thermometer (Traceable® Digital Thermometer, Control Company, Friendswood, Texas 77546 USA) to monitor and control the temperature in the impregnation vessel. After impregnation at time intervals of 1, 4 and 12 h- at each of the specified temperatures; Room Temperature (R.T.), 40, and 60 ^{o}C, the pieces were removed and placed in liquid N_2 (-180^{o}C) to stop (minimize) the further migration of Li^+. Due to the rapid freezing rate, an eventual effect of the migration of Li^+ ions, as the freezing front moves inwards, was minimized. These frozen pieces were then placed in a freeze dryer (LABCONCO®, Kansas City, MO, USA) for about 2 weeks, to avoid any secondary thermal diffusion. In order to determine whether the wood pieces were fully freeze-dried or not; one extra wood piece was also processed during the entire procedure together with the wood pieces on which the measurements were performed and placed in the freeze drier. This extra wood piece was periodically weighted until it reached the uniform weight; thereby ensuring the completeness of the freeze drying process.

5.4 Flame Atomic Emission Spectroscopy (FAES) Analysis

In preparation for the Li^+ ion concentration measurement, each of the impregnated wood pieces was cut into small cubes (Figure. 5.4).

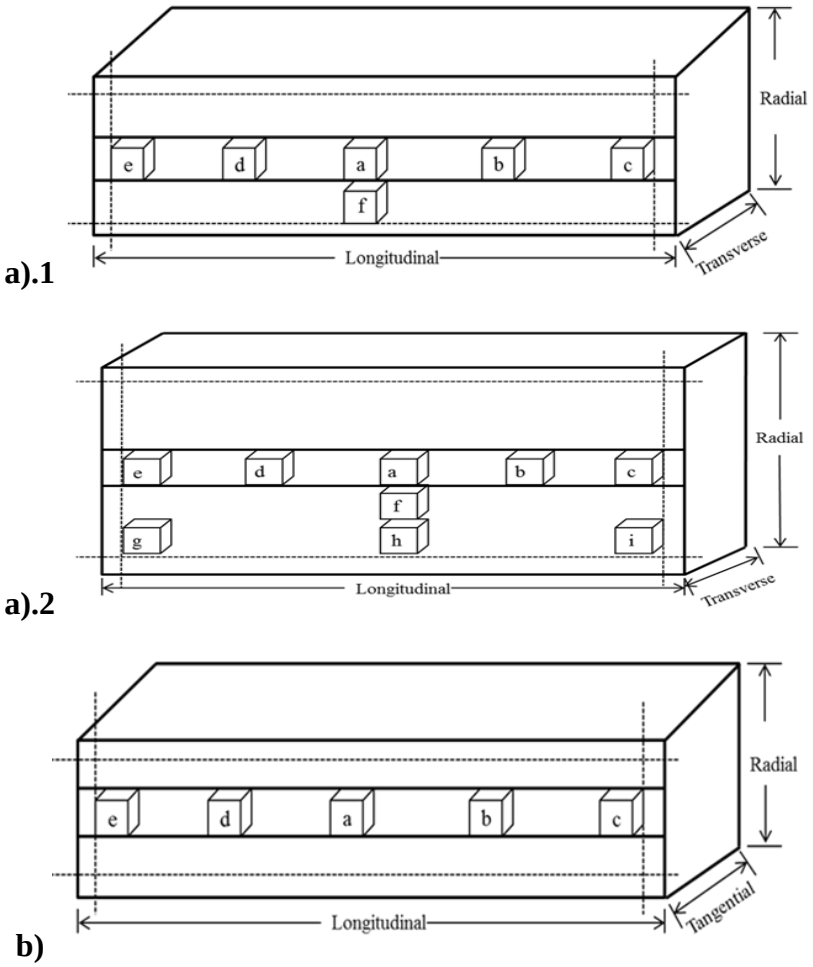

Figure 5.4 Selection of small cubes with dimensions (as indicated in the text) from an idealized wood piece: in experiments with normal wood pieces and at R.T.-**a).1** 100x25x8 and **a).2** 100x50x4 mm^3; in all the experiments with surface-smoothed wood pieces with dimensions 100x22x5 mm^3- **b).** These cubes were microtomed into slices of ~ 0.3 mm thick for Li^+ concentration profile measurements.

Small cubes were prepared using the same vertical band saw machine as mentioned above. The targeted cube dimensions were approximately: a) in experiments with normal wood pieces and at R.T. -10x10x8 and 10x10x4 mm^3 in 1 h impregnation experiments and 5x5x8 and 5x5x4 mm^3 in 4 and 12 h impregnation experiments, b) in all the impregnation experiments with surface-smoothed wood pieces -6 x 6 x 6 mm^3. Each cube was microtomed in the tangential direction to slices of ~ 0.3 mm thickness which were oven-dried at 105^oC for 1 h to remove any accumulated moisture during the microtoming process. Following the drying, the wood slices were placed in desiccators containing blue gel salt and at R.T. until reaching constant mass was reached. Each of these slices collected into a sampling bottle with 2 wt% HNO_3 (Nitric acid) (Mallinckrodt Baker, Inc. Phillipsburg, NJ, USA) solution, as the leaching liquor. The leaching was performed at R.T. for about 24 hours. To ensure that equilibrium had been reached after 24 h of leaching time, a set

of leaching experiments was conducted for 72 h of leaching time. The results showed that there was no difference in the release of Li^+ ion between 24 and 72 h of leaching time. At the end of the leaching period, the leaching liquor was collected with a syringe connected to 0.45 µm PVDF (PolyVinyliDeneFluoride) membrane filter (Pall Life Sciences, Ann Arbor, MI, USA). Thereafter the leaching liquor was analyzed for Li^+ ion concentration using Flame Atomic Emission Spectroscopy (Thermo Scientific, iCE 3000 series, AA spectrometer; Cambridge, United Kingdom). An air-acetylene torch was used as the flame source, and the emission was measured at a wavelength of 670.8 nm. The Li^+ ion concentration was kept at the optimum working concentration range of 0.02 to 5 µg/ml.

6. RESULTS AND DISCUSSION

This chapter presents the results obtained from studies conducted so far. The following abbreviations are used in the text below: NWP (Normal Wood Pieces) means wood pieces that were carefully prepared from a stemwood disc, using a vertical band sawing machine; and SsWP (Surface smoothed Wood Pieces) means, wood pieces that were carefully planed on all 4 vertical surfaces to peel off the damaged surface layer of NWP at a depth of about 0.5 to 1.5 mm using a hand plane.

The density profiles were also determined in addition to the main concentration profiles. The parameter density is important because earlywood and latewood have different densities, which affect the transport of ions. In our methodology, the density of a dried wood slice is defined as the ratio of the oven-dried weight of a wood slice to the volume of the freeze-dried wood slice. The density profiles were estimated for cube **a** (cf Fig 5.4) of both Sapwood (Sw) and Heartwood (Hw) samples with two dimensions (Fig. 6.1). As expected, earlywood and latewood show lower and higher densities, respectively (Jyske et al., 2008). However, the density variation in Hw is not consistent compared with Sw due to its different chemical composition; for example, the extractive content in Hw is higher.

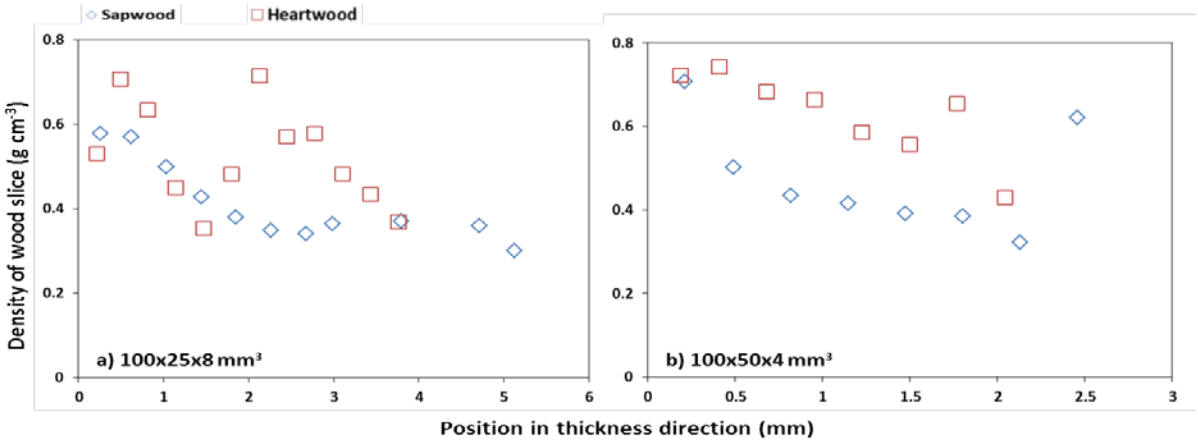

Figure 6.1 Density profiles for cube **a** (cf Figure 5.4) of both Sw and Hw samples at room temperature : a) 100x25x8 mm^3 piece, and b) 100x50x4 mm^3 piece.

The uniformity of the bulk LiCl concentration in the impregnation vessel was measured at four different time intervals during all of the chemical impregnation experiments. The results indicated that, in all experiments with 1, 4, and 12 h of treatment times at room temperature, the wood pieces were uniformly exposed to the bulk concentration of 7±0.5 (g Li^+ L^{-1}) [1 M LiCl = 6.98 g Li^+ L^{-1}] . As well for the chemical impregnation experiments at 40 ^oC, the wood pieces were exposed to the bulk concentration of 7±1 (g Li^+ L^{-1}) in all experiments with 12 and 4 h of treatment times. Likewise for the chemical impregnation experiments at 60 ^oC, the wood pieces were exposed to the bulk concentration of 7±0.5 (g Li^+ L^{-1}) in all experiments with 4 and 12 h of

treatment time. In a similar way, the temperature inside the impregnation vessel was continuously monitored and recorded at four different time intervals during the chemical impregnation experiments: observations indicated that the temperature inside the impregnation vessel was maintained at 40 ±1 ^{o}C for the experiments at 40, and 60 ±1 ^{o}C for the experiments at 60 ^{o}C.

As the concentration of the chemical agent at the center of the wood piece is a reasonable measure of the completeness of the wood treatment, most of the data reported in this chapter are the results for the cube **a**, which is from the center portion of the wood piece (cf Fig. 5.4). In all of the concentration profiles presented in this chapter, the concentration (g of Li^{+} L^{-1}, where L is the free volume of a dried wood slice) is plotted against the position in the thickness direction of the wood piece. These data describe the diffusional mass transport, i.e. the assumption is that the mass transfer occurs through lumens and pits filled with water. The concentration at zero mm has been assumed to be equal to the concentration of the LiCl bulk solution in the impregnation vessel, which is an average value of the measured concentration at four different time intervals during the chemical impregnation experiments.

6.1 Error analysis of the experimental methodology

In order to investigate the reproducibility of the experimental methodology used, the Li^{+} ion concentration profiles were measured for 3 different SsWP prepared from Sw with similar specifications in dimensions (~ 100x22x5 mm^3), after 12 h of chemical impregnation experiments at 40 ^{o}C. In Figure 6.2, it can be seen that two (wood piece 1 and 2) of the three experimental runs show good similarities in Li^{+} ion concentration profiles with an experimental error of about 7 %.The third (wood piece 3) experimental run shows that several data points largely deviated and this behavior can be assumed to be due to cracks in the wood structure. If all data points (wood piece 1, 2, and 3) are considered in the calculation of the experimental error, the error turns out to be quite large, about 27%, but if some of the data points that may be considered to be erroneous due to faults (micro-cracks) in the 3 wood pieces are excluded from error calculations, the error decreases to about 9%. This is a good example of one of the advantages of local measurements, since it is apparently quite easy to detect different defects such as micro-cracks in the wood pieces used.

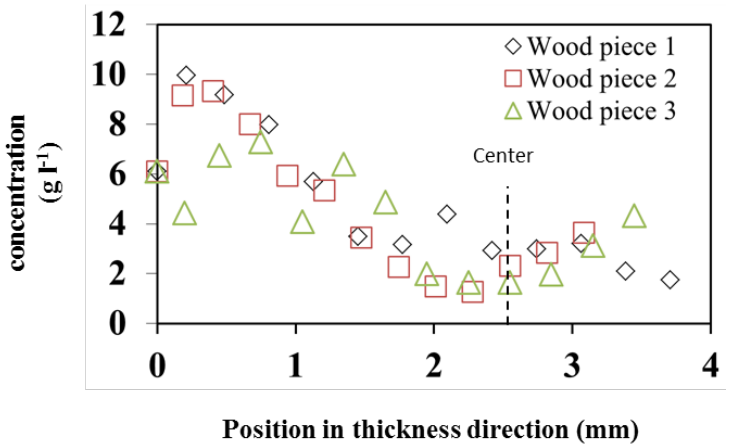

Figure 6.2 Measured Li^+ ion concentration profiles in 3 different SsWP prepared from Norway spruce Sw with dimensions 100x22x5 mm^3 after 12 h impregnation time at 40 ^oC.

6.2 Concentration profiles at various locations in a single wood piece

Figures 6.3-6.8 show the concentration profiles for different positions (a, b, c, d, and e cf Fig.5.4). The differences in concentration profiles at various locations are due to the fact that mass transport properties were strongly influenced by the anisotropy of the wood samples. Here it is evident that the concentration profiles for cube **a** (middle) and cube **b**/cube **d** (between the middle and the edge of the piece) were quite similar: in these two cases the diffusion of Li^+ ions was only influenced by mass transport in the transversal direction. However in the case of cube **c**/cube **e** (at the edge of the piece), the concentration profile is different and in this case the diffusion of Li^+ ions was also influenced by mass transport in the longitudinal direction in addition to the transversal direction. This observation is more pronounced in Sw than in Hw, with longer impregnation time and higher temperature. These differences in Sw and Hw concentration profiles are due to differences in structural and chemical compositions of Sw and Hw, e.g. a) Hw is usually much less permeable than Sw due to pit aspiration and incrustation in it (Siau, 1984), and b) the extractive content in Hw is higher than in Sw. However, different shapes in the concentration profiles were observed for extended impregnation times as well as at higher temperatures. This is probably due to the remaining effect of micro-cracks on Li^+ ion diffusion in the wood samples.

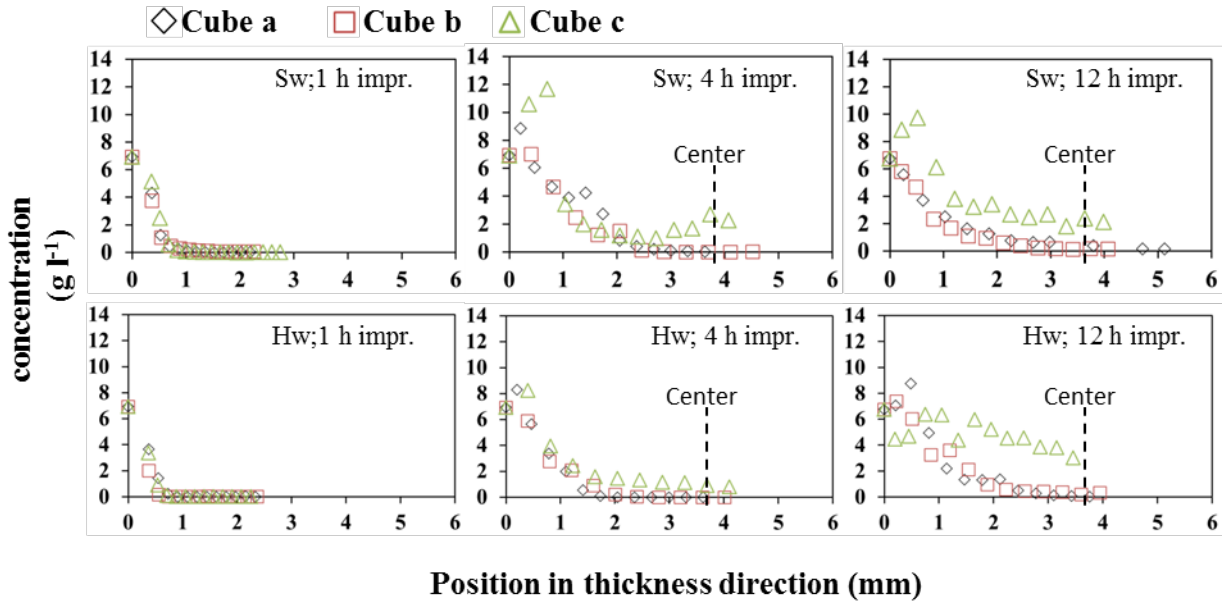

Figure 6.3 Measured Li^+ ion concentration profiles in Norway spruce NWP with dimensions 100x25x8 mm^3 from Sw and Hw at **room temperature** for 1, 4, and 12 h impregnation times (as indicated). Cubes a, b, and c refers to the sampling within the wood pieces (cf. Figure 5.4.a).1).

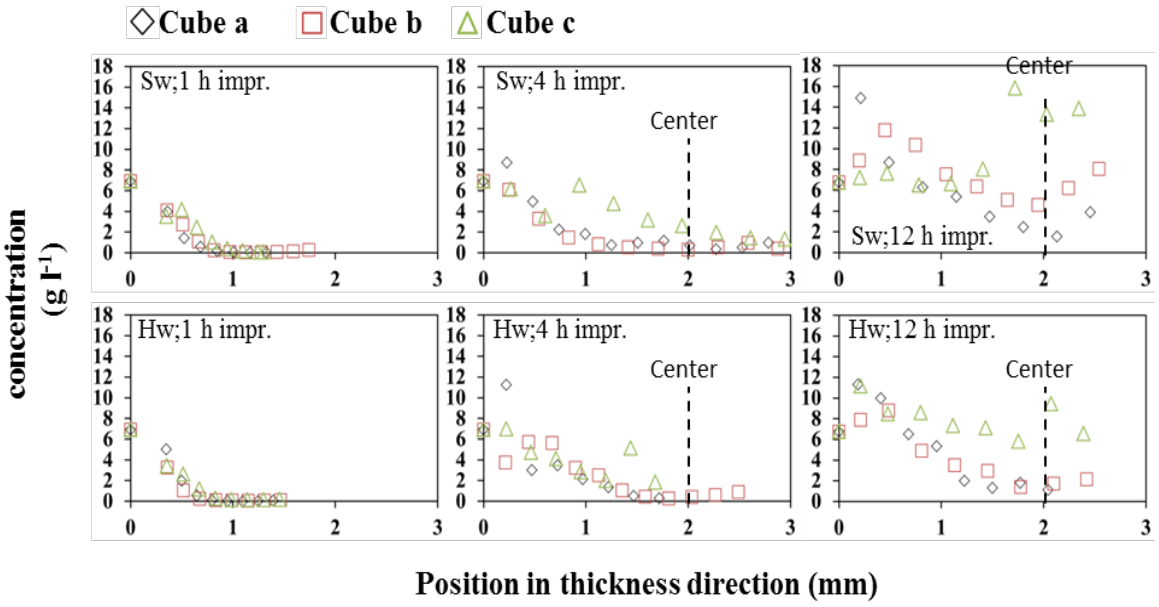

Figure 6.4 Measured Li^+ ion concentration profiles in Norway spruce NWP with dimensions 100x50x4 mm^3 from Sw and Hw at **room temperature** for 1, 4, and 12 h impregnation times (as indicated). Cubes a, b, and c refers to the sampling within the wood pieces (cf. Figure 5.4.a).2).

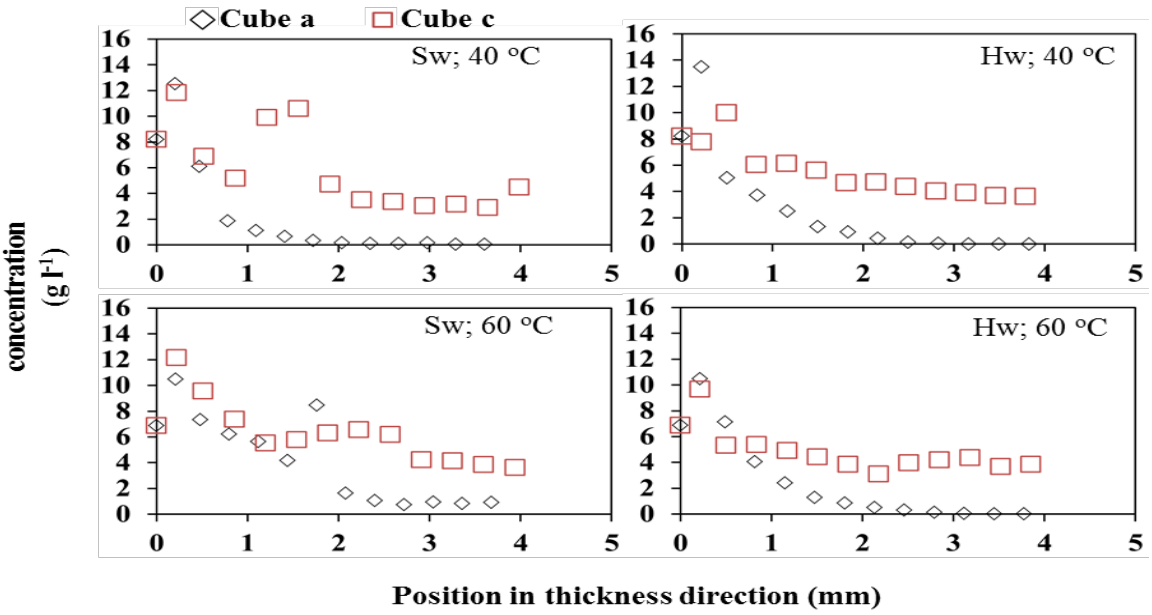

Figure 6.5 Measured Li^+ ion concentration profiles in Norway spruce NWP with dimensions 100x25x8 mm^3 from Sw and Hw at **40** and **60 °C** (as indicated) for 4 h impregnation time. Cubes a and c refers to the sampling within the wood pieces (cf. Figure 5.4.a).1).

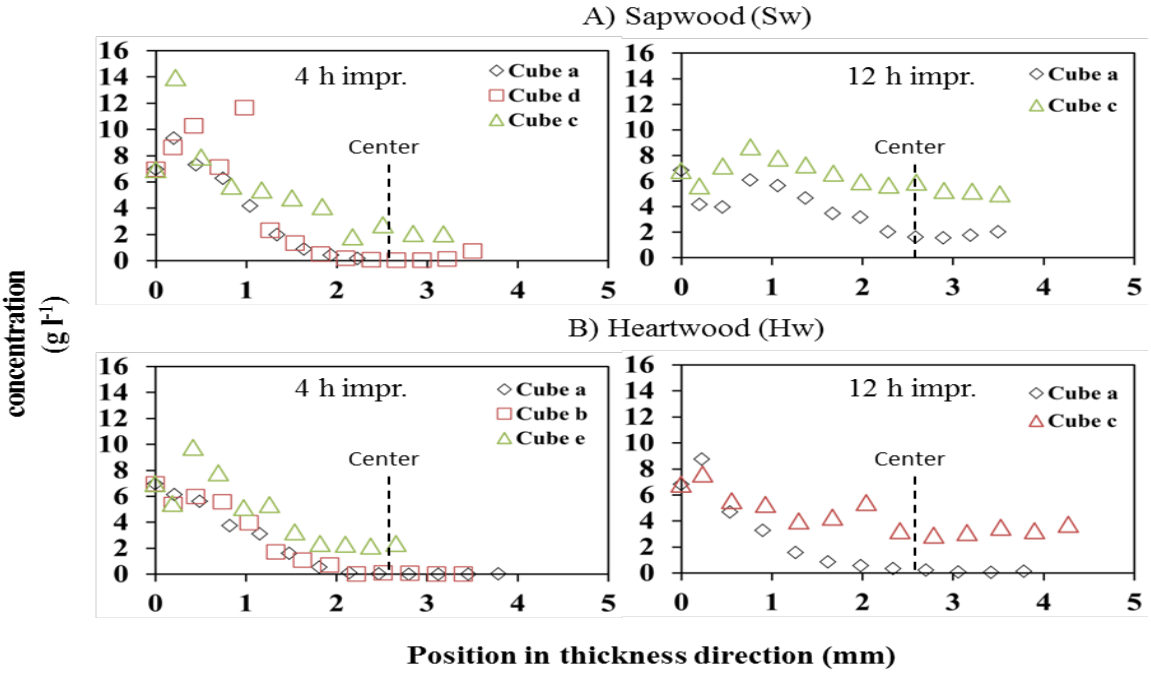

Figure 6.6 Measured Li^+ ion concentration profiles in Norway spruce SsWP (100x22x5 mm^3) at various locations within a single wood piece; after 4 and 12 h impregnation experiments (as indicated) conducted at **room temperature**-A)Sw and B) Hw. Cubes a, b/d, and c refer to the sampling within the wood piece (cf Figure 5.4.b)).

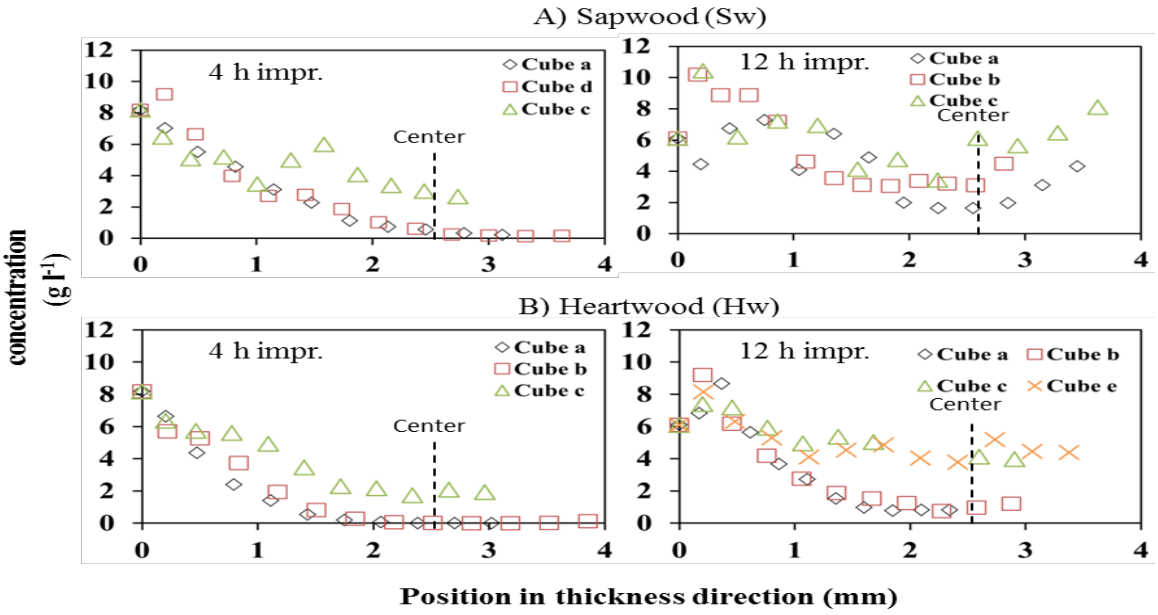

Figure 6.7 Measured Li^+ ion concentration profiles in Norway spruce SsWP (100x22x5 mm^3) at various locations within a single wood piece; after 4 and 12 h impregnation experiments (as indicated) conducted at **40 °C**-A) Sw and B) Hw. Cubes a, b/d, and c refer to the sampling within a wood piece (cf Figure 5.4.b)).

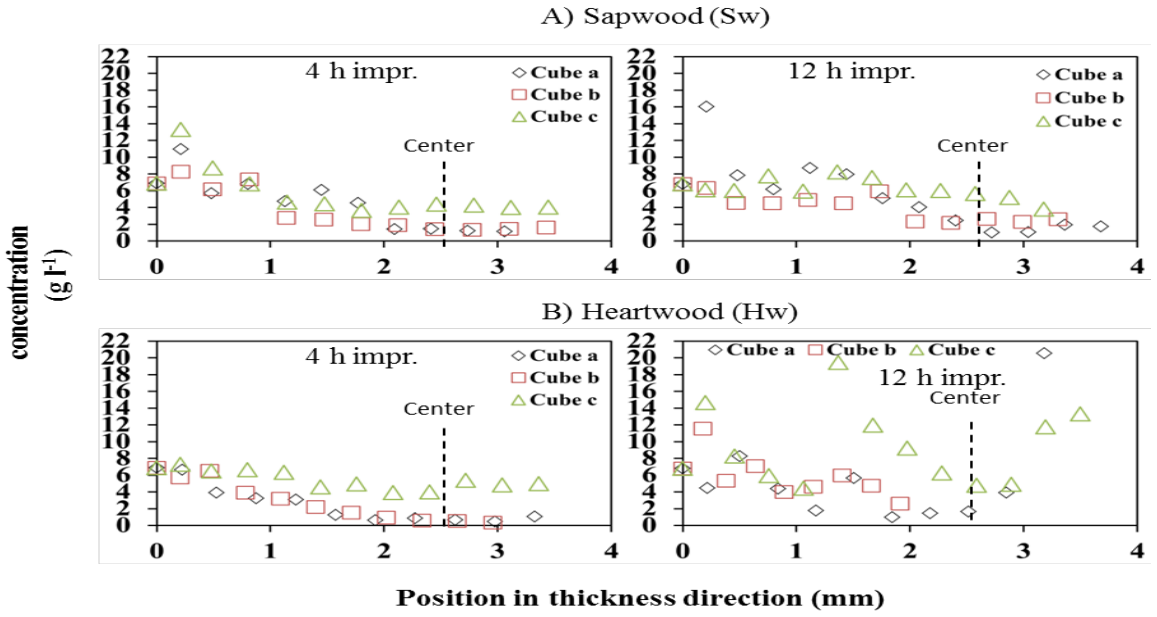

Figure 6.8 Measured Li^+ ion concentration profiles in Norway spruce SsWP (100x22x5 mm^3) at various locations within a single wood piece; after 4 and 12 h impregnation experiments (as indicated) conducted at **60 °C**-A) Sw and B) Hw. Cubes a, b/d, and c refer to the sampling within the wood piece (cf Figure 5.4.b)).

6.3 Effect of various parameters on Li^+ ion concentration profiles in Norway spruce

In order to measure the concentration profiles as a function of wood piece dimensions, impregnation time, temperature, and wood structure, the effect of various parameters on the Li^+ ion concentration profiles in Norway spruce wood has been evaluated.

6.3.1 Effect of impregnation time

Increased Li^+ ion concentration was observed at the corresponding positions in the thickness direction of the wood pieces as the impregnation time increased (Figures 6.9 and 6.10). In the chemical impregnation experiments at different temperatures, a shift in concentration profiles towards the center of the wood piece was visible as the impregnation time increased. This phenomenon was more pronounced in Sw than in Hw samples, and with increasing temperature (Figures 6.10 A) and B)). However, at 60 ^oC, the effect of impregnation time on concentration profiles for both Sw and Hw samples was small but different behavior in the concentration profiles was observed (Figure 6.10 C)). Moreover, the observation of a higher Li^+ ion concentration in the eluate of slices from the outer-most surface layer than in the bulk solution was also more pronounced in Sw than in Hw, as the impregnation time increased, and as the impregnation temperature increased. This phenomenon may be the result of an ion exchange equilibrium caused by the ionic groups present in the wood fiber wall. Similarly, Kuitunen, S et al., (2013) have demonstrated that the molality of cations is higher in the fiber wall liquid than in the liquid external to the fiber wall, due to ion exchange equilibrium phenomena. Thus the increase in ion concentration that occurs on the outer-most surface layers of wood pieces may be explained by the Donnan equilibrium theory. Although the effect of micro-cracks on Li^+ ion concentration profiles is much smaller in experiments with SsWP (Figure 6.10) than in experiments with NWP (Figure 6.9), it seems that the effect of micro-cracks on concentration profiles remains to some extent and contributes to the different shapes in the concentration profiles at extended impregnation times as well as at higher temperatures (Figure 6.10 C)).

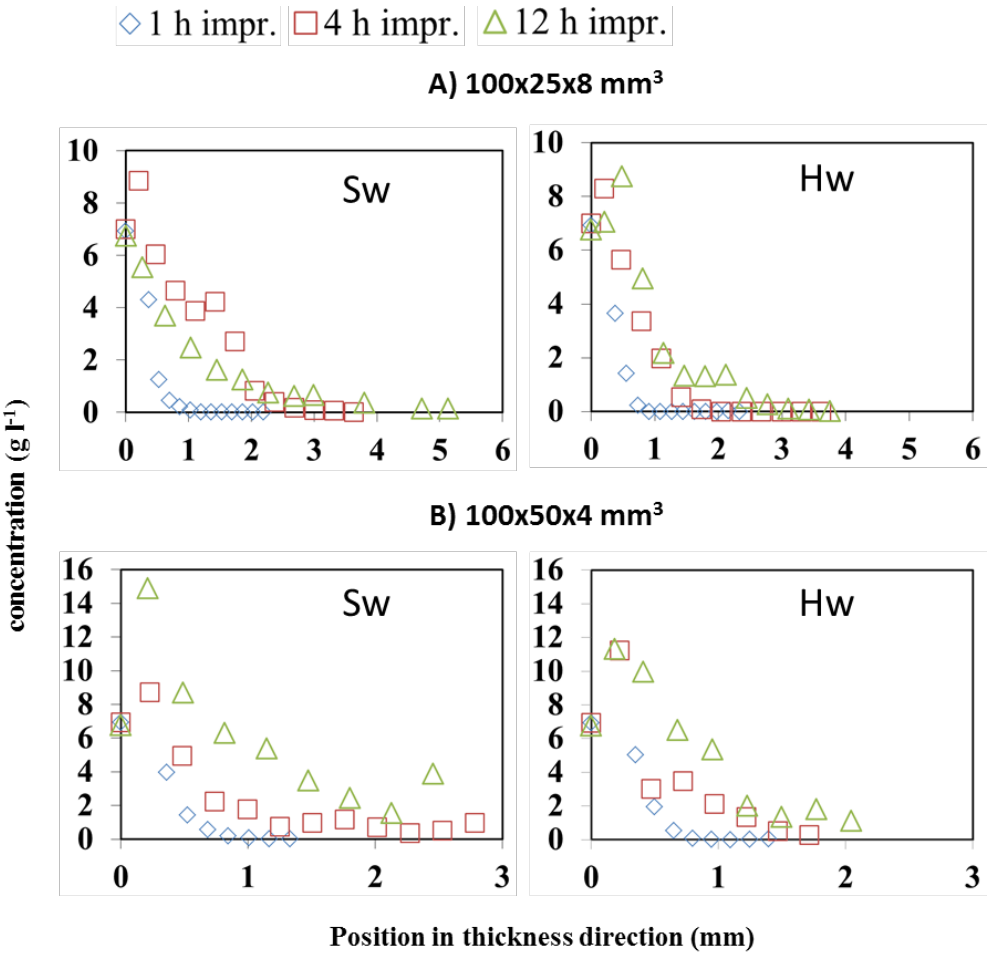

Figure 6.9 Measured Li^+ ion concentration profiles in NWP prepared from Norway spruce Sw and Hw samples as a function of impregnation times (as indicated) at room temperature: A) 100x25x8 mm^3, and B) 100x50x4 mm^3.

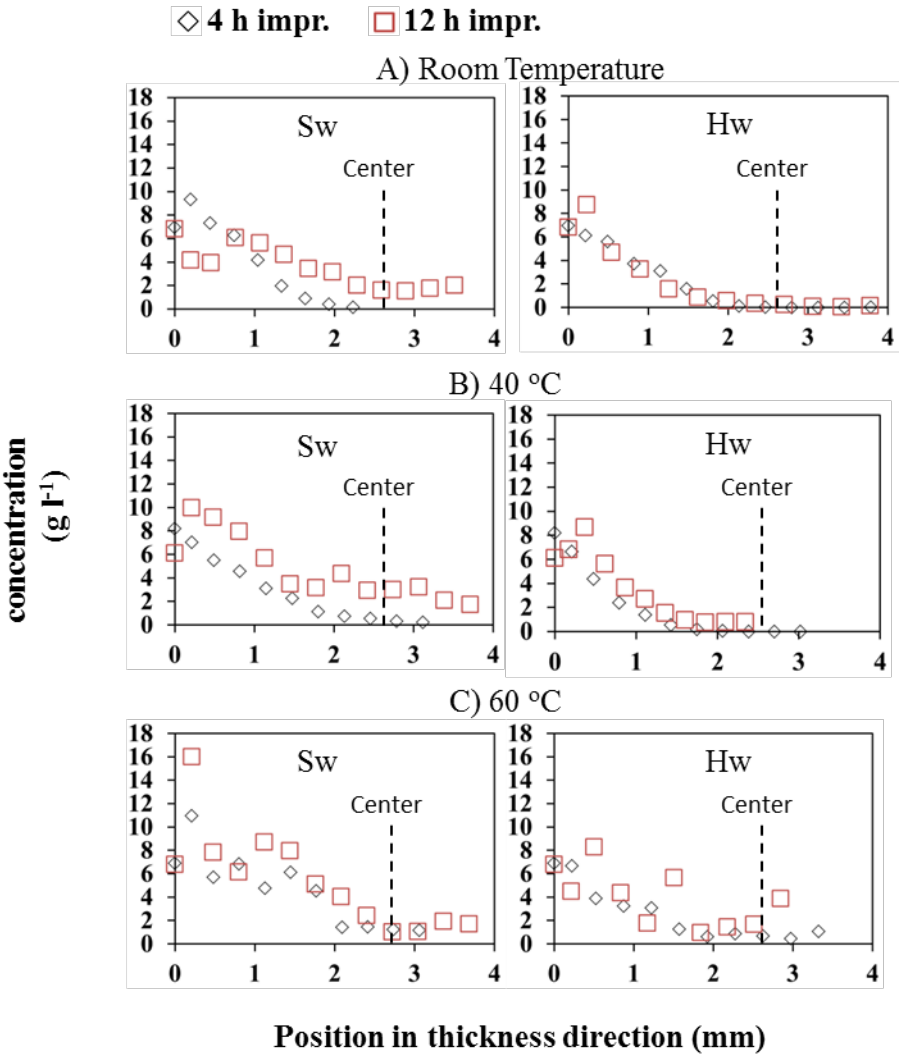

Figure 6.10 Measured Li^+ ion concentration profiles in SsWP with dimensions 100x22x5 mm^3 prepared from Norway spruce Sw and Hw samples as a function of impregnation times (as indicated) at A) Room temperature, B) 40 ^oC, and C) 60 ^oC.

6.3.2 Effect of wood structure and wood piece dimensions

A similar Li^+ ion concentration profile was observed in both 4 as well as 8 mm thick pieces from both Sw and Hw samples of Norway spruce after a short impregnation time of 1 h (Figure 6.11 a)). The concentration profiles show that there was a mass transport of Li^+ ions into the wood pieces. The difference in Li^+ ion concentration between Sw and Hw samples was within the experimental error for 1 h impregnation time at room temperature for both dimensions of the wood pieces. However, it should be kept in mind that the penetration depth observed in this study was less than 1 mm. Thus, the similarities between the concentration profiles indicate that the properties of the wood pieces close to the surface are similar, which may be explained by changes in the wood material close to the surface that may have occurred during the preparation of the

wood pieces. These changes may be, e.g. the formation of many small cracks, invisible to the naked eye, but sufficient in number to affect the mass transfer of Li^+ ions.

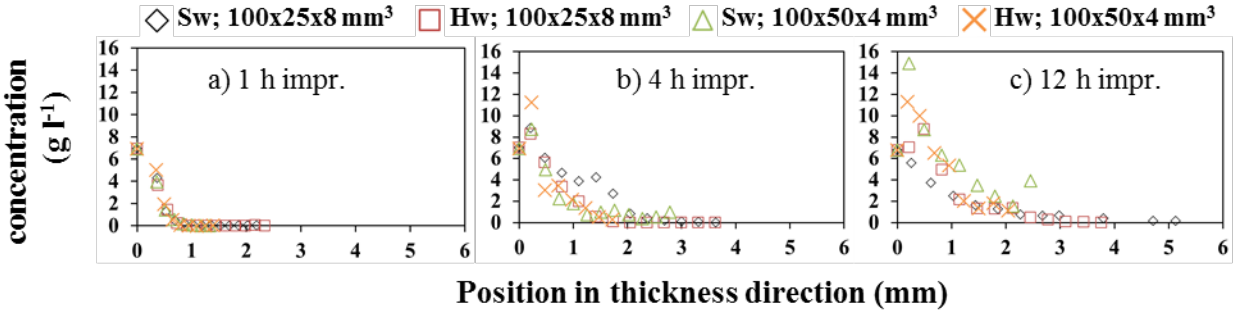

Figure 6.11 Measured Li^+ ion concentration profiles in Norway spruce NWP at room temperature: Sw vs. Hw; and 100x25x8 mm^3 vs. 100x50x4 mm3; for impregnation times of a)1 h, b)4 h, and c) 12 h.

After longer impregnation times the Li^+ ion concentration profiles shifted towards the center in wood pieces with the thickness 4 and 8 mm (Fig 6.11 b) and c) vs. a)). The shapes of the concentration profiles of the 4 mm thick pieces are approximately what can be expected in a diffusional operation. However, the concentration profiles of the 8 mm thick pieces have a different shape. One possible reason is that micro-cracks present in the pieces may contribute to increased accessibility for Li^+ ions to diffuse further into the interiors of the wood pieces with longer impregnation time. This is one example of why measuring local concentrations is more reliable than methods based on average properties: With this methodology it is possible to detect faults (defects) in the wood pieces which are not possible to detect if the method based on average properties is used.

It is also evident that after 1 and 4 h impregnation times, the 4 mm thick pieces have more similar concentration profiles than the 8 mm thick pieces, which can be expected since the concentration in the center had not yet been changed. However, after 12 h impregnation time, there is a tendency that the concentration profiles for the 4 mm thick pieces have slightly higher concentrations than the 8 mm thick pieces. This can be readily explained by the fact that the concentration levels at the center of the 4 mm thick pieces had increased, i.e. the ions had reached the center of the 4 mm thick pieces which was not the case for the 8 mm thick pieces.

6.3.3 Effect of method of preparation of wood pieces

In this section several illustrations of observations are presented to indicate the influence of damaged surface layers on Li^+ ion concentration profiles in Norway spruce wood samples. In Figure 6.12, a higher Li^+ ion concentration can be seen in the outer most surface layers in NWP than in SsWP. This is a clear indication that the rough surface layers, which were formed during the rough sawing process, may have altered the mass transfer and effect of Donnan equilibrium on Li^+ ion diffusion in NWP more than in SsWP. Figure 6.12, shows that the outer most surface

layer, which is 1-2 mm, may have different properties compared to the bulk of the wood piece. Therefore it seems that the formation and behavior of the damaged surface layers depends on the method of preparation of the wood pieces. Moreover, it was observed that the effect of the damaged surface layer on Li^+ ion diffusion in Norway spruce Sw was more pronounced than in Hw. Even though the effect of the damaged surface layers on the Li^+ ion concentration profiles in Norway spruce wood was minimized by peeling off the damaged surface layers of the NWP using a hand plane (SsWP), the defects remained and exhibited different behavior in the concentration profiles at extended treatment times and higher temperatures (e.g. Fig. 6.12 d)).

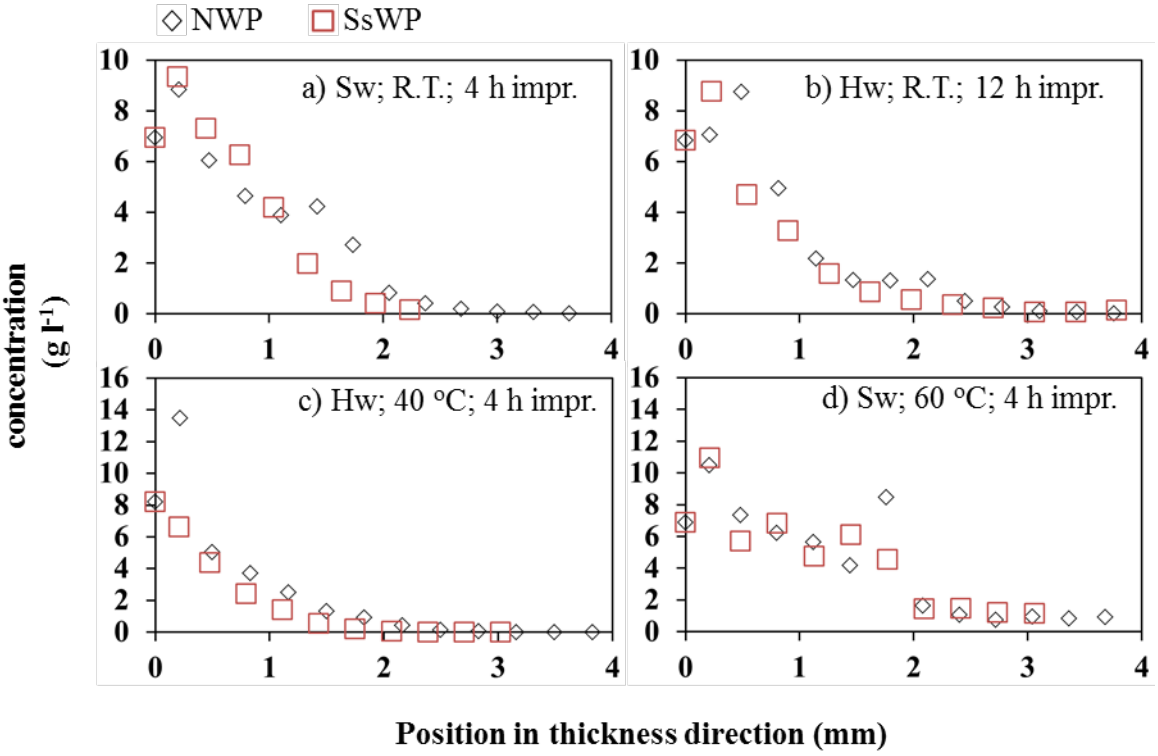

Figure 6.12 Measured Li^+ ion concentration profiles in Norway spruce Sw and Hw samples and at different temperatures (as indicated) and for impregnation times: NWP vs. SsWP; a)Sw; R.T. (Room Temperature); 4 h, b)Hw; R.T.; 4 h, c)Hw; 40 ^oC; 4 h, and d)Sw; 60 ^oC;12 h.

6.3.4 Effect of temperature

Only minor differences between the Li^+ ion concentration profiles were observed as the impregnation temperature increased (Figures 6.13 and 6.14). As expected, a shift in the Li^+ ion concentration profile is visible toward the center as the impregnation temperature increased. This observation is more pronounced in Sw than in Hw and with increasing impregnation time from 4 to 12 h (Figure 6.14 A)). A shift in concentration profiles towards the center of the wood piece is also noticeable as the impregnation temperature increased (Figure 6.14 B) over extended

treatment times (12 h). However the difference observed is minor and within the experimental error. On the other hand, the calculated Li^+ ion concentration profiles (See Appendix) in a prototype plane sheet using self-diffusion coefficients of Li^+ ion (Figure 6.15), show a clear and increased effect of temperature at longer treatment times (12 h) as compared with shorter treatment times (4 h). These differences in the effect of temperature on Li^+ ion concentration profiles between the wood material a plane sheet prototype (Figure 6.13&6.14 vs. Figure 6.15) indicates that the ion transport in wood material may also be influenced by other phenomena such as surface diffusion, adsorption/desorption, and Donnan equilibrium.

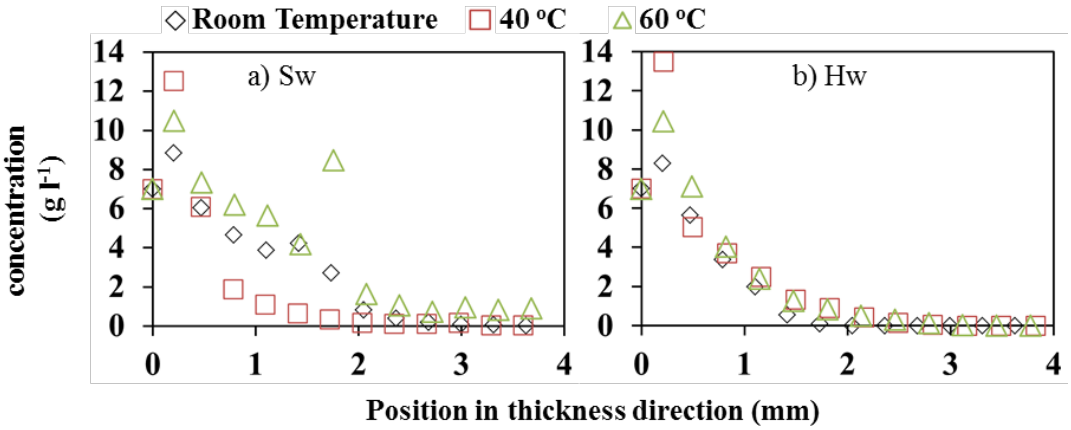

Figure 6.13 Effect of temperature on Li^+ ion concentration profiles in NWP of Norway spruce with dimensions of 100x25x8 mm^3 after 4 h impregnation time for a) Sw and b) Hw samples.

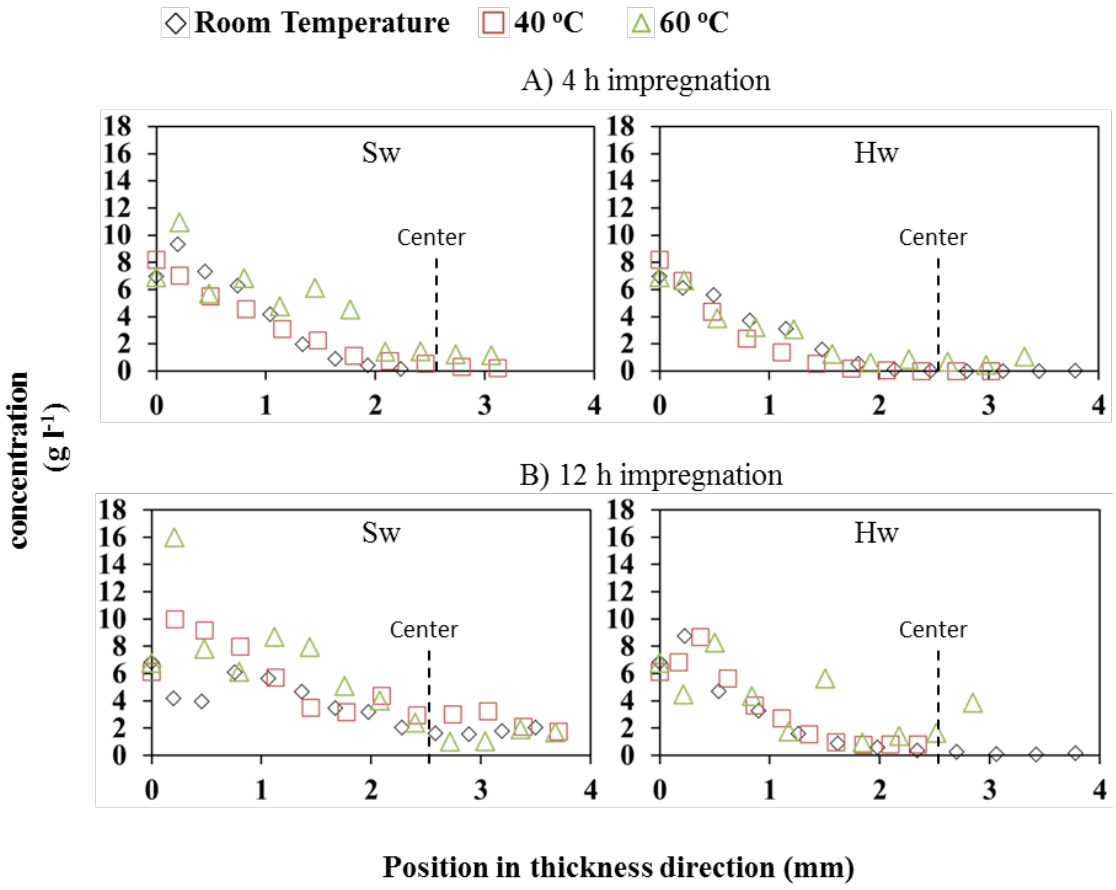

Figure 6.14 Measured Li^+ ion concentration profiles in SsWP 100x22x5 mm^3 prepared from Norway spruce Sw and Hw samples as a function of impregnation temperature (as indicated) after impregnation for A) 4 h, and B) 12 h.

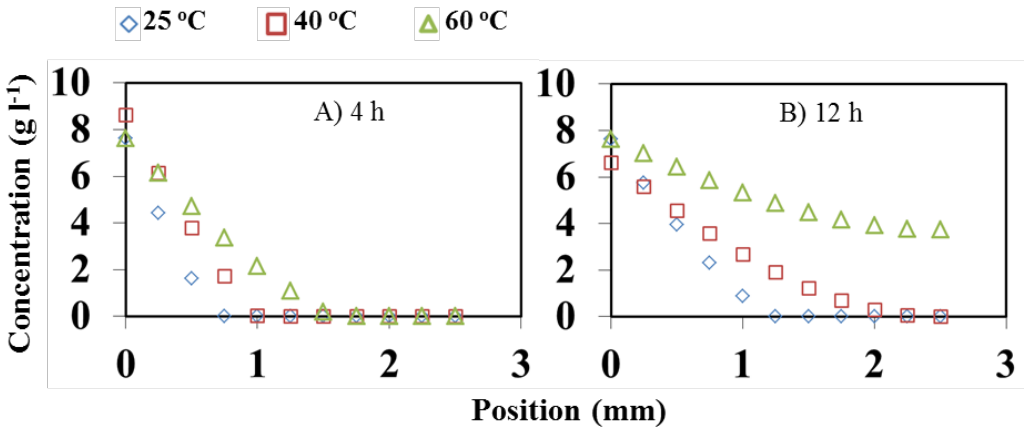

Figure 6.15 Predicted Li^+ ion concentration profiles in a plane sheet of 5 mm thick as a function of temperature (as indicated) for times A) 4 h, and B) 12 h.

7. CONCLUSIONS

- Eventhough the proposed methodology is time consuming, traditional Flame Atomic Emission Spectroscopic (FAES) determination of Li^+ ion concentrations in the eluate of slices taken from different positions is precise.
- The methodology gives local concentration profiles, which are needed in order to obtain a deeper understanding of the mass transport in wood
- This method is a sensitive, and thus facilitates detecting if there are any defects (micro-cracks) in the wood pieces used.
- For the experimental conditions chosen, the effects of temperature and differences between Sw and Hw on Li^+ ion concentration profiles in Norway spruce wood observed were less significant than the effect of impregnation time.
- The Donnan effect was observed in the slices taken from the outermost surface of the wood pieces and this phenomenon varied as a function of treatment time, temperature as well as between Sw and Hw.

8. PROPOSALS FOR FUTURE WORK

- Further improvement of the proposed experimental methodology would entail evaluating the effect of Donnan equilibrium on measurements of Li^+ ion concentration profiles in Norway spruce wood in order to calculate the precise diffusivity constants.
- The effect of wood anisotropy on measurements of Li^+ ion concentration profiles in Norway spruce wood must be evaluated in order to verify the validity of the diffusional mechanism separately in two different directions (longitudinal and radial).
- The diffusivity for the system would be calculated by fitting a model based on first principles, using commercial software tool e.g. COMSOL multiphysics.
- The diffusional behavior of other industrially important Scandinavian wood species such as Pine and Birch should be studied.

9. APPENDIX- Effect of temperature on predicted Li^+ ion concentration profiles in a plane sheet

From the experimental value of the self-diffusional coefficient of Li^+ ion in 1 M LiCl aqueous solution at 25°C (Braun and Weingärtner, 1988), and the viscosities of 1 M LiCl solution at different temperatures (Wimby and Berntsson, 1994), the self-diffusion coefficients of Li^+ ion at different temperatures were calculated using the following equation (Eqn. 6.1) (Poling et al., 2001) and tabulated in Table 6.1:

$$D_{Li^+}^{T°C} = D_{Li^+}^{25°C}\left(\frac{T°C}{25°C}\right)\left(\frac{\mu_{LiCl}^{25°C}}{\mu_{LiCl}^{T°C}}\right) \tag{9.1}$$

Where, $D_{Li^+}^{T°C}$ is the self-diffusion coefficient of Li^+ ion, and $\mu_{LiCl}^{T°C}$ is the viscosity of the 1 M LiCl solution at temperature T.

Table 9.1 Viscosities of 1 M LiCl solution and self-diffusion coefficients of Li^+ ion in 1 M LiCl solution at different temperatures.

Temperature (T, in °C)	Viscosity (μ, in pa.s) of 1 M LiCl solution	Self-diffusion coefficient of Li^+ ion (D_{Li+}, in m^2/s)
25	$5x10^{-3}$	$0.924x10^{-9}$
40	$3.58x10^{-3}$	$2.065x10^{-9}$
60	$2.47x10^{-3}$	$4.49x10^{-9}$

For the diffusion of a solute into a plane sheet with initial and boundary conditions, Fick's second law of diffusion (Eqn. 3.3) can be rearranged to Equation 9.2 by performing a Laplace transform (Crank, 1970). In Equation 9.2, the Li^+ ion concentration in the plane sheet is given as a function of the position in the plane sheet, time, diffusion coefficient, initial boundary concentration, and for constant concentrations on both surfaces.

If $C = C_1$, $z = 0$, $t \geq 0$;

$C = C_2$, $z = l$, $t \geq 0$; and

$C = f(z)$ (initial distribution), $0 < z < l$, $t = 0$;

The solution in the form of trigonometrical series is

$$C = C_1 + (C_2 - C_1)\frac{z}{l} + \frac{2}{\pi}\sum_{1}^{\infty}\frac{C_2\cos n\pi - C_1}{n}\sin\frac{n\pi z}{l}\,exp^{(-Dn^2\pi^2t/l^2)} + \frac{2}{l}\sum_{1}^{\infty}\sin\frac{n\pi z}{\pi}\,exp^{(-D\pi^2n^2t/l^2)}\int_0^l f(z')\sin\frac{n\pi z'}{l}\,dz' \tag{9.2}$$

In this case the initial concentration gradient of Li^+ ion in the plane sheet is assumed to be zero i.e. f (z) = 0.

In Equation 9.2,

C = Li^+ ion concentration in the plane sheet at a certain position z after time t (g L^{-1})

$C_1 = C_2$ = Surface concentrations at the sheet-LiCl solution boundary for all t, this is the bulk LiCl solution concentration which is ~7 g L^{-1}.

z = position in the plane sheet, measured from the LiCl-plane sheet boundary (m)

t = time (s)

D = diffusion coefficient (m^2/s)

l = thickness of the plane sheet (m) which is 5 mm

Equation 9.2 was used to predict the Li^+ ion concentration profiles in a plane sheet for known Li^+ self-diffusion coefficients at different temperatures (Table 9.1) and for different treatment times.

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